Chem Ed

EDITORIALLY SPEAKING

Are textbooks going to lose their hard covers? is a question that is being asked seriously by many. No observer on a college campus can fail to be impressed by the large number of paperbacks, many of them pocket-size, which he sees on bookstore shelves and in student hands. In 1958, 13% of all college textbooks were bound in paper, a figure twice that of 1954. The revolution that the paperback has produced in the teaching of humanities subjects is almost phenomenal. Seldom does the college student of today read merely about Plato—or nibble at him from anthologies. A freshman owns a personal copy of "The Republic" and is expected to read it. Assignments of collateral reading no longer need to be preceded by a careful consideration of the logistics with a librarian.

What effect is the paperback surge having on the conduct of chemistry courses? Not much, is our guess. Nor do we expect very much in the future. It is very doubtful that a textbook which gets as much of a workout as does the typical chemistry text could last a semester without a hard cover. Certainly the cost of producing a new book in paperbound form would be so close to that for the hardbound one that the small saving to the student would vanish with the frayed and falling pages.

The interesting speculation about possible changes in the future is that chemistry professors too, may begin to assign more collateral reading. Even if they do not, the true scholars among their students may discover the wealth of scientific literature that is beginning to show up on the shelves devoted to paperbound books. Until recently the only volumes on such shelves that had any relevance to science were those on the philosophy or history of science. In this field an almost complete library of the classics as well as more recent critiques of the classics can be assembled.

Now hardly a month goes by during which we are not able to spot titles of books dealing directly with chemical topics in the lists of paperback publishers. For years Dover Publications has been making it possible for chemists to own many of the classics of physics, biology, and medicine. The works of Planck, Darwin, Oparin, Herzberg, Bernard, Osler, and many others can be economically in the library of the student.

Recently McGraw-Hill has inaugurated a paperback series of reprints. Chemistry professors can rediscover and students can be introduced to such pedagogic best-sellers as Farrington Daniels' "Mathematical Preparation for Physical Chemistry" ($2.50), Anderson's "Chemical Calculations" ($2.75), or Margenau's "The Nature of Physical Reality" ($2.50).

Harper's Torchbooks, in addition to its impressive list on the history and philosophy of science (Dampier, Sarton, Bronowski, and Einstein to name a few), is giving chemists some wished-for titles: Findlay's "Chemistry in the Service of Man," Partington's "Short History of Chemistry," and Read's "Direct Entry to Organic Chemistry." Reading "From Atomos to Atom" by Van Melsen, also a Torchbook, will provide students with a sense of continuity and depth in scientific ideas that few courses can give.

The ten-volume series of Scientific American Books (Simon and Schuster) now includes not only "Physics and Chemistry of Life" but a fascinating collection of papers on the theme "New Chemistry"—reactions, methods, elements and compounds.

The Science Study Series (Doubleday-Anchor) includes at least two titles appropriate for reading by chemistry students. "Crystals and Crystal Growing" covers the subject from the elementary school project level to solid state theory. C. V. Boys' 1902 classic, "Soap Bubbles," is another entertaining yet profound conversation that will send even sophisticated Ph.D. chemists to the kitchen to experiment.

"Understanding Chemistry" by L. P. Lessing (Mentor) can be used by students at all levels. This former editor of *Fortune* and *Scientific American* combines perspective, knowledge, and knack for writing to produce a story that reads like a novel and should go far to give students an appreciation of how chemistry has gotten where it is, where it is going, and why.

Finally, mention should be made of "The Chemical Elements" (Science Service-Ballantine), originally compled by Helen Miles Davis and revised by Seaborg. This pocket-sized giant not only serves as a convenient handbook-type compilation of information, but also provides (in English) excerpts from original papers announcing the discovery of each element. There are few better bargains anywhere for chemists.

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Alfred Nobel

The annual awards of the Nobel Prizes for outstanding achievements in physics, chemistry, medicine, and literature, as well as the Peace Prize, continuously perpetuate the name of Alfred Nobel. The splendor and the solemnity of the occasions when the prizes are presented to the laureates in Stockholm and in Oslo in the presence of the Royal Family, members of the Government, of the Diplomatic Corps, representatives of Swedish and Norwegian institutions, and the intellectual world of the countries, reminds us of the European culture of the late nineteenth century, based as it was on considerable prosperity and in some instances on really outstanding wealth. In these the darkest days of the year around December 10, the anniversary of Alfred Nobel's death, when nobody would like to go to Stockholm, except possibly to receive a Nobel prize, the capital of Sweden is the center for the biggest scientific and literary event of the year. University people all over the world comment upon the awards, and the newspaper men find an opportunity to suggest a number of candidates for the Peace Prize and the prize in literature, much more worthy of getting the prizes than the laureates of the year. All the civilized world is for a moment paying attention to the Nobel Prizes and to their founder.

The Nobel Family

The name Nobel is not derived from the latin word *nobilis*, but from a place named Nöbbelöv in the South-Swedish province of Scania. One of Alfred Nobel's ancestors, Petrus Olofsson, born 1655 in Nöbbelöv, went as a young man to study in the Swedish university town of Uppsala. Having been entered in the university register under the name of Petrus Olai Nobelius, the ambitious young man completed his education in law and married a daughter of the famous university chancellor Olof Rudbeck, Sr., who in his younger days (1653) had discovered the lymph vessels and the thoracic duct simultaneously with Bartholini.

The family, though introduced into influential circles and endowed with good hereditary genes, did not become prosperous. (At the time of Alfred Nobel's birth, his father went bankrupt!) The son of Petrus Nobelius was an artist, whose income did not match his standard of living. His youngest son, Immanuel, Sr., only three years old at his father's death, later took up medicine but never had the opportunity to complete his studies. As a military surgeon living in the town of Gäfle, he cut off the academic touch of the name changing it to Nobel.

His son, Immanuel, Jr., born in 1801, the father of Alfred Nobel, was an outstanding personality. He was an inventor of genius with a quite unusual vitality. After receiving an incomplete technological education in Stockholm, he established himself as a building constructor, contractor, and inventor. Very soon, however, he started building beyond his means and also had a large part of his work destroyed by fire. In 1833 he went bankrupt. In order to avoid imprisonment he moved in 1837 to Finland then under Russian rule, outside of Swedish jurisdiction and soon to Russia where he established himself as a mechanical engineer in St. Petersburg. His wife joined him there five years later, together with their two youngest sons, Ludwig, eleven years old, and Alfred, nine.

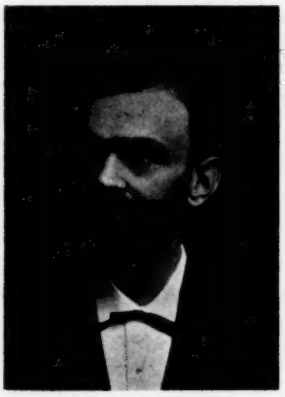

Figure 1. Alfred Nobel.

In his workshop in Petersburg, Immanuel Nobel made wagon wheels, steam hammers, and other tools. But his chief interests soon became explosive mines. In the beginning the Russian government could not reach any decision about using his mines. It could not be decided where the mines belonged, whether the Army or the Navy should procure them.

When the Crimean war was imminent, the government supplied Nobel with a subsidy for the extension of his factory, and when the war broke out in 1854 the Russian High Command entrusted the mine-laying program to Nobel. Kronstadt, the fortress Sveaborg in Finland, and the harbor of Reval in Estonia were all protected with mines. Immanuel Nobel had thus rendered the Russian government very great services. For this, although a foreigner, he was awarded an Imperial gold medal in 1853.

But Russia is Russia. The Crimean war ended in

[1] Editor's Note: The selection of Nobel Laureates in physiology and medicine is one of the duties of the faculty of Karolinska Institutet. The scientific world salutes this institution in 1960 on the occasion of the 150th Anniversary of its founding.

defeat. The old tsar Nicolaus I had passed away. The new government disregarded the promises made by its predecessor and placed no orders of any kind in Nobel's enterprises, but to the contrary supported his competitors. As a consequence Nobel's workshop went bankrupt and he himself, broken down and disappointed, returned in the same year, 1859, to Stockholm almost as poor as when, twenty-two years ago, he left the shores of Sweden.

Alfred Nobel was born in 1833 at the time of his father's first bankruptcy. His only formal education consisted of three terms at the elementary school of Jacob's parish in Stockholm at the age of eight. (In Russia the three brothers, Robert, Ludwig, and Alfred, were instructed by a private teacher, who, judging from his pupils' success as linguists and engineers later in life, must have been a first class pedagogue.) The education ended when Alfred was sixteen years of age. He then had an opportunity of visiting the United States for a short period and of travel in Europe for a couple of years, partly in order to improve his health.

Through his father Alfred had been introduced into the field of explosives, and he found many important problems awaiting solution. One of them was the employment of nitroglycerin as an explosive.

Nitroglycerin

In 1833 the French chemist Braconnot in Nancy succeeded in nitrifying starch and cellulose by dissolving them in concentrated nitric acid. The product, called "xyloidine" was insoluble in water but soluble in ether-alcohol and was violently combustible. Four years later, his compatriot Pelouze dipped paper in strong nitric acid for a time, washed it, and obtained the first nitrocellulose, "pyroxyline," which he suggested might find a practical application in the case of artillery. Schönbein at Basel, who in 1846 nitrated cellulose with a mixture of nitric and sulfuric acid, demonstrated that his "gun-cotton" was much more efficient than ordinary gunpowder in firearms and artillery pieces and for blasting operations in mines. Simultaneously Professor Böttiger of Frankfurt made similar experiments. Schönbein's material was successfully demonstrated in blasting experiments in the Cornish mines.

In 1847 an Italian, Sobrero, a pupil of Pelouze's, prepared nitroglycerin, "piroglycerina." He stayed with Pelouze 1840–43 and visited Liebig in Giessen for a few months before returning to Turin, where he lived as a teacher and professor of chemistry until 1883.

Owing to the high risk of explosion, this new compound was very difficult to handle. On the one hand it burned like an oil without explosion when directly ignited and on the other could explode at any time during storage or if handled carelessly, particularly if the product was insufficiently purified and still contained nitric and nitrous acid. Thus, nitroglycerin remained a taboo for technicians for 18 years after its invention. Alfred Nobel succeeded in getting the fluid to detonate at will and in exploiting its power.

In Russia in 1862 he had placed nitroglycerin in a firmly stoppered glass tube inside a metal tube filled with black powder and had ignited the latter by means of a fuse. The whole was thrown into a canal and caused a heavy underwater explosion.

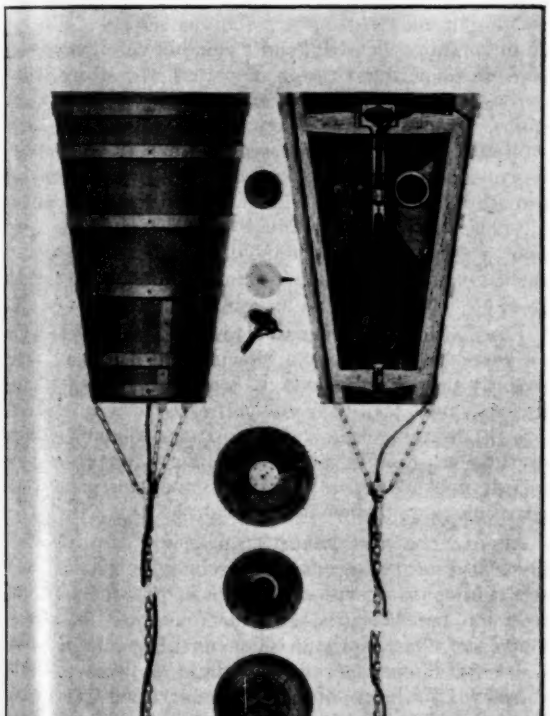

Figure 2. Submarine mine, as designed by Immanuel Nobel.

Nobel's Detonator

In 1863 Alfred went to Stockholm to join his father in the work with nitroglycerin. Here he repeated his Russian experiments but put the components in reverse order.

Instead of putting a tube of nitroglycerin into a larger tube filled with gunpowder, he dipped a small tube of gunpowder, with a fuse attached to it, into a large tube of nitroglycerin. This gave excellent results. On igniting the black powder by means of the fuse, the nitroglycerin exploded, developing its full blasting power.

Nobel's "Patent Detonator" was discovered, Alfred Nobel's greatest invention which revolutionized the whole techique of explosives and was the most important contribution to the subsequent development of the high explosives industry.

The detonator itself was a very simple device, a small wooden cylinder about two inches long containing a tightly sealed charge of ordinary gunpowder with a fuse attached to it. New and more efficient detonators like fulminate of mercury were later found, but the principle remained the same. This is considered to be the greatest invention of its kind after the invention of black powder.

When the nitroglycerin was placed in a closed iron pipe, an explosive cap was obtained which worked under water. The first underwater experiments with

explosives were, as mentioned, made in St. Petersburg, and in 1863 Alfred Nobel received the first Russian patent on his new blasting technique. In 1864, after receiving a Swedish patent for the manufacture and use of nitroglycerin, he and his father, who was still actively engaged in the experiments, organized a small laboratory for the production of pyroglycerin at Heleneborg in Stockholm.

The interest in the new blasting technique was tremendous. The state railways and various mining companies soon realized the possibilities presented by Nobel's patented blasting oil and began using it immediately. In 1864 it was used for blasting the tunnel under the southern island of the city of Stockholm, Södermalm, when the main southern railway line was led into the capital.

Nitroglycerin Explosions

During this period a series of severe accidents occurred in his newly-erected factories. Careless handing of the material due to ignorance of the risks involved led to terrible explosions.

The first serious accident occurred in Sweden in 1864, when Nobel's Heleneborg laboratory in Stockholm blew up on September third. On this occasion Alfred's youngest brother, Emil, an engineer, was killed.

A Hamburg paper of December 4, 1865, contained a comprehensive description of such an explosion which happened in New York. In a small hotel in Greenwich Street a German traveler had left a demijohn carefully wrapped in a box, containing 10 lb of nitroglycerin, which he said he would fetch later. The box was left with the porter and was used alternatively as a seat and as footrest in boot-polishing. One Sunday morning a waiter noticed that red fumes were issuing from it. The porter carried it out into the street and returned to the hotel. The next moment there was a terrible explosion, destroying the fronts of the neighboring houses, breaking windows and doors, and tearing up the street to a depth of four feet.

Other devastating explosions occurred in Panama, San Francisco, Australia, and in Nobel factories in Germany and in Belgium. These terrible accidents almost threatened to nullify the first great discovery in the explosive field. World opinion had become perturbed over the numerous accidents caused by the nitroglycerin.

The authorities of the city of Stockholm declared after the Heleneborg explosion that if Alfred Nobel wanted to go on with the manufacture, he could do it on a barge anchored in Lake Mälaren, and do it by himself. And this Alfred Nobel did.

Of course nobody was interested in placing money in such a risky enterprise as the manufacture of nitroglycerin. Already at the end of 1864, however, a millionaire, J. W. Smitt, of Stockholm took the economical responsibility for the Nobel enterprise when in 1865 a factory could be erected on solid ground again at Vinterviken near Stockholm.

During 1864 and the beginning of 1865, Alfred had taken over the direction of everything concerning tests, production, and exploitation of the new explosive in Sweden. When the Nitroglycerin Company was formed he seems to have been simultaneously managing director, production manager, chief clerk, and cashier. The company's first cashbook was kept by him personally in the autumn of 1864. In spite of the heavy blow that had descended upon the family through the explosion at Heleneborg, he maintained his faith in his discovery and its future with admirable courage.

Dynamite

In the meantime Alfred Nobel experimented intensively in order to make nitroglycerin less dangerous. He mixed it with sawdust, powdered cement, and charcoal. His efforts finally led to the discovery of dynamite, blasting oil adsorbed by kieselguhr. The diatomaceous earth, a readily available raw material, took up three times its weight of nitroglycerin. The nitroglycerin was thereby stabilized but still exploded on detonation. The dynamite could be safely handled, packed in cartridge form, transported, and stored without risk. As a powder it could be filled in bore holes from which the liquid blast oil would have run out. In 1867, in Sweden, this second great discovery was patented which in combination with the earlier detonator provided the first rational technique for the use of explosives. In 1868 Immanuel and Alfred Nobel were jointly awarded the Letterstedt Prize of the Swedish Academy of Science, an honor in which Alfred set great store all his life. It was his Nobel Prize.

Figure 2. Nobel's laboratory at Bofors, Sweden. The building is still preserved in its original shape.

From now on the situation was changed. What for 18 years had been only a chemical curiosity and had recently threatened to become a real danger to humanity, was now transformed by the technically trained Nobel family into one of the most evolutionary factors of the age, making possible mining enterprises previously unheard of, and railway, tunnel, and canal constructions, e.g., the tunnels through the Alps.

Alfred Nobel now spent his time in continuous traveling from country to country, for the establishment and supervision of factories and for the acquisition and protection of patent rights. Now he found use for his cosmopolitan education and solid knowledge of the chief European languages, and last but not least, for his detailed knowledge of the manufacturing processes. He had talent enough to build a world-wide organization with the capacity for producing the necessary amounts of explosives. During the years 1867 to 1874 the world production of dynamite rose from 11 to 120 tons a year.

In spite of these activities a new discovery followed in 1875. It was the blasting gelatin, also called rubber dynamite, in which 7 per cent of low nitrated cellulose or collodion was dissolved in 93 per cent of nitroglycerin forming a viscous semisolid mass. The mixture was not so voluminous as dynamite, had a greater blasting power, and was totally consumed on ignition.

Ballistite

The next patent was on smokeless gunpowder, the "Ballistite" or the Nobel gunpowder, in which nitroglycerin was mixed with an equal part of guncotton (nitrocellulose). Nobel found that by increasing the proportion of nitrocellulose from 7 to 50 per cent and kneading the mixture between heated rollers he could obtain a bricky substance which could be pulverized to a powder. Contrary to the blasting gelatin it exploded less violently and thereby developed a propellant ballistic force when used in firearms without splitting the barrel. The blasting power of nitroglycerin had been ameliorated. This invention of a propellant explosive, made in 1887, later came to be of the greatest importance for the progress in the manufacture of ammunition for firearms and ordnance pieces. His Ballistite competed successfully in various countries with the French Poudre B of Vieille, which was nitrocellulose gelatinized by means of volatile solvents and with the British Cordite, a slight variation of Nobel's Ballistite.

The Cordite Law Suit

In England Nobel had met with no success in his attempts to get a license for manufacture. Partly there was the insular prejudice against embarking on any enterprise due to foreign initiative. But the main obstacle he could not overcome was Sir Frederick Abel, an adviser of the House of Commons on matters of explosives who exerted considerable influence in keeping Nobel's nitroglycerin away from England. He himself was interested in Schönbein's nitrocellulose, guncotton, which he had made less unstable through washing away acids from it with water.

In 1869 a Nitroglycerine Act was introduced, forbidding the import, storage, and transport of that substance in the country. Only in 1871 was Nobel licensed to erect a nitroglycerin factory in Scotland.

Nobel came into serious conflict with the two inventors of Cordite, the physicist James Dewar and Sir Frederick Abel. At the request of a government commission, Nobel had informed Dewar and Abel, who were members of the commission, about all the details concerning the patented procedure of manufacturing Ballistite. Nevertheless Dewar and Abel added vaseline to Nobel's nitroglycerin and nitrocellulose mixture, dissolved it in acetone, so that the mass could be drawn out in threads, and patented the product under the name of Cordite. Nobel felt compelled to take legal action against them. On the ground that the plaintiff, Nobel, had spoken about the "well known soluble nitrocellulose" in his claims and the defendants had used the insoluble variety of nitrocellulose, Nobel lost the case. The law suit cost him 30,000 £, and it reduced almost to nil the value of the Ballistite patent.

One of the judges of the Court of Appeal, Lord Justice Kay, expressed his doubts regarding the justice of the decision. He honored Nobel by citing the old sentence that the dwarf who stands on the shoulders of a giant obviously should see farther than the giant himself. "I have in this case," he said, "my sympathies with the original inventor. Mr. Nobel made a great invention, a principally new and extraordinary thing—and then two clever chemists in reading his description discover that they can use the same starting material with only a small difference in one of the components for getting a similar product with exactly the same properties. In fact through our decision Mr. Nobel has been deprived of an extremely valuable patent." In order to ameliorate the injustice, the Nobel's Explosive Co., which made the Cordite for the British Government, paid Nobel a royalty even on its manufacture of Cordite, amounting to half the amount it paid for the Ballistite per kilo.

A benevolence of that kind would, if it had been shown to Nobel in the U.S.A., have made the Nobel Prizes twice as large as they are now, or still larger. In spite of the enormous use of dynamite in the New World, Alfred Nobel benefited very little from it. His fights with the country's unscrupulous financial racketeers, on which he lost much time, were very disappointing to him. The story of his hopeless fight is vividly told by Herta Pauli in her book on Alfred Nobel of 1942 (*1*), and by Robert Shaplen (*The New Yorker*, March 15 and 22, 1958). According to Pauli, Nobel lost all interest in his American business. After 1866 he did not cross the Atlantic, and he never exchanged as much as a letter with the two giant companies making dynamite over there or with any other businessman in the United States.

How close the ties were between Alfred Nobel and the British enterprises in the explosive field was demonstrated in 1918 when the British Explosives industry was unified in a single organization, called Explosives Trades, Ltd. The organization soon found that the name Nobel signified quality in the industrial world and therefore changed its name to Nobel Industries, Ltd.

Nobel Refineries at Baku

A very interesting chapter in the history of the Nobel family is the part played by Robert. He had married a Finn and moved to Helsingfors, where he ran a lamp and oil shop. His idea of "enlightening the faithful Finnish people" became, however, a financial failure. After a visit to Sweden, where he learned how to make nitroglycerin, and an attempt to introduce the product in Finland, he returned to Russia in 1870 and three years later traveled down to Caucasia, on behalf of his brother Ludwig, in order to buy Russian walnut wood for the rifle butts for his brother's arms factory. This was the beginning of the world-wide naphtha industry of the Nobel families. During his stay in Baku, the practical engineer and former lamp and oil trader was impressed by the great possibility of exploiting the Russian naphtha, which in unlimited amounts freely poured out of the earth in the neighborhood of Baku.

Two years later he returned and started extracting petroleum from the oil. In 1877 the Russian state monopoly on raw oil was abolished and a territory was sold to the newly formed company of the Nobel broth-

ers, Robert and Ludwig. Now the family's engineering knowledge and technical talent became useful. Within a short time they had created a world industry.

Alfred Nobel became a member of Nobel's Oil Company in 1878 and stabilized it by large capital investments. But he never found much time for this enterprise. Nor did he count on the possibility of making nitroglycerin in Russia. His father's experience had taught him never to rely upon the Russian order of government. The outside world gave him a sufficiently large field for work. It must, however, be properly admitted that Alfred Nobel's continuous fear that his shares in the Baku enterprise and his claims on the company amounting to four million rubles, should be lost, did not prove correct. The value of his holding in the Nobel Brothers Naphtha Company was paid in cash by the Russian branch of the family to the executors of his will to the benefit of the Nobel Foundation.

Alfred Nobel's Personality

In the biography, edited by the Nobel Foundation in 1926 under the direction of Schück and Sohlman (*2*), it is said of Nobel's private life, that he once was jokingly characterized as Europe's richest tramp. Undoubtedly, these words contained a certain amount of truth.

During the hectic years after his invention of the detonator he traveled from country to country. Mostly he lived in the vicinity of Hamburg, and later in Paris, where at 59 Avenue Malakoff he had a three-story house. Sweden, however, still remained his home-country, and here he chose his collaborators among whom the foremost was the engineer Alarik Liedbeck.

Alfred Nobel never married. All his life he suffered from poor health. The bills for doctors and medicine for Alfred played a considerable part in the economy of the family during the earlier days. When things changed for the better heavy business obligations occupied all his time. It is said that the king, Charles XII of Sweden, remained a bachelor because of the difficulty of carrying a queen with him on his endless war expeditions in Russia, Poland, and Turkey. The same applies to a certain extent to Nobel. There was also the difficulty of finding an intellectually equal partner; he could not even find a secretary who mastered languages perfectly enough to satisfy his demands.

When his brother Ludwig once asked for biographical information about their father and Alfred himself, the latter answered:

"Why do you want to torment me with biographical essays? No one reads essays except about actors and murderers, preferably the latter, whether they have carried out their impressive deeds at home or in the field of battle."

. . . "Important things and contractual duties nowadays lie waiting on my desk for weeks, even months, owing to lack of time. In such circumstances it is quite impossible for me to write biographies if they are not as short as a police description, but these are, I think, the most eloquent. For example: Alfred Nobel, a poor semi-alive creature, who should have been suffocated by the doctor as he, with a yell, made his entry into life. His greatest merits: to keep his nails clean and never be a burden to anybody. Greatest fault: to lack a family, good temper, and good stomach. His greatest and only demand: not to be buried alive. Greatest sin: not to worship Mammon. Important events in his life: none."

Nobel and the Peace Movement

During the first twenty years following his discovery of the detonator in 1863–64 and of dynamite in 1867 Alfred Nobel's activities were exclusively limited to the manufacture of nitroglycerin and dynamite, including the rubber dynamite of 1875 and their application in the fields of mining and in road, canal, and tunnel constructions. Some of the most remarkable improvements in traveling conditions had been achieved. Nothing could be more misleading than to label Alfred Nobel as a "merchant of death," as has been done. His fortune was collected during these first twenty years.

It was not until the middle eighties with the discovery of the Ballistite in 1887 that the question about the use of his products in firearms and in artillery became a reality. From then on the purely military aspects came into the foreground. Nobel's Ballistite had to compete with Vieille's Poudre B in France and with Dewar and Abel's Cordite in England. In a number of countries the Nobel Powder was used in the Army and Navy, e.g., in Italy, but not in France. In line with these interests was his taking over the Bofors-Gullspång Company in Sweden in 1894.

Being highly intellectual and strongly influenced by the humanistic tendencies of contemporary literature, and with a keen eye for the weaknesses of the political systems of his time, Alfred Nobel could not avoid getting involved in the discussion about war and peace. His discoveries had opened unlimited possibilities for destructive wars, and the big powers cultivated a hostile attitude toward each other. Nobel declared that the European culture would perish in war, unless a reliable peace agreement could be reached within the next thirty years. "If in thirty years we shall not have succeeded in reorganizing the world, it will inevitably relapse into barbarism."

Nobel himself thought that the only chance of peace lay in the opposing powers hesitating before the risks involved. When Bertha von Suttner, who in 1889 published "Lay Down Arms," asked for money for the Peace Congress in Bern in 1892, she received a sum, but Nobel did not believe that the Congress could be of any particular value. "I believe," he said, "that my factories will put an end to war sooner than your Congresses. When the day dawns, that two army corps can destroy each other in one second, all civilized nations will surely recoil from war in horror and disband their armies." At least, he said, the governments would postpone hostile actions for a year or two, hoping that the air would clear in the meantime, some politicians might possibly die, and common people would have time to think it over before starting the bloody business. If this should fail an international court and a collective defence system should be applied against an aggressor. "Wars will become impossible when all states bind themselves absolutely to take action against the first aggressor."

Even if Nobel did not trust very much in the efficiency of peace congresses he finally decided to design the Peace Prize in his will "for the person who shall have done the most effective work for promoting friendly relations between the peoples, for the abolition or reduction of standing armies and for the formation and

popularization of peace congresses." Being a practical man he fully understood that the best way of putting dynamite under the war mongers was to create friendly relations among the inhabitants of neighboring countries, a principle successfully applied for the first time in the history of Europe 9 years after his death, when the union between the Scandinavian brother-countries Sweden and Norway was dissolved. It was an intelligent step Nobel took when he put the awarding of the Peace Prize in the hands of the Norwegians, the "rebels" who urgently demanded to have the union with Sweden broken.

The Will

When Nobel, in the nineties, felt that it was time to write his will and dispose of a fortune amounting to 33 million Sw. crowns, he decided that the money should be used for the benefit of society.

The witnesses to the will later said that they had heard him say on the occassion of signing:

"At heart I am a social democrat, in moderation. I especially believe large inherited fortunes to be a misfortune, which only serves to stupefy humanity. A person who owns a large fortune should, therefore, only allow a small part of it to fall to his relatives."

He considered it wrong to leave even direct heirs more than they need for education, or to let them have a larger sum than they have earned themselves. To act differently, he thought, would mean encouraging indolence and preventing a healthy development of the individual's capacity to create an independent position for himself.

The content of his will is very well known. He stated that

"The capital thus secured shall constitute a fund, the interest accruing from which shall be annually awarded in prizes to those persons who shall have contributed most materially to benefit mankind during the year immediately preceding. The said interest shall be divided into five equal amounts, to be apportioned as follows: One share to the person who shall have made the most important discovery or invention in the domain of Physics; one share to the person who shall have made the most important Chemical discovery or improvement; one share to the person who shall have made the most important discovery in the domain of Physiology or Medicine; one share to the person who shall have produced in the field of Literature the most distinguished work of an idealistic tendency; and, finally, one share to the person who shall have most or best promoted the Fraternity of Nations and the Abolishment or Diminution of Standing Armies and the Formation and Increase of Peace Congresses."

Nobel made up his will and signed it on November 27, 1895. It is known that his distaste for lawyers was so great that even on this exceptional occasion he refused to ask for legal advisers; consequently many formalities were overlooked. Because of his distrust of all lawyers Nobel did not succeed in expressing clearly his intentions in his will.

Nor were the governing bodies who should award the Prizes asked beforehand if they were able or willing to accept the offer. It thus happened that the Swedish Academy of Science, which now awards the prizes for physics and chemistry, felt unable to select representatives even for preliminary discussions with the executors of Alfred Nobel's will until it was evident that the will would become legally recognized. Leading conservative politicians in Sweden declared the will as an infringement of the legal rights of Nobel's heirs.

Meanwhile some of Nobel's heirs in Sweden had brought an action against the executors, claiming that the will should be declared invalid. The executors of the will appointed by Nobel, Mr. Ragnar Sohlman and Civ. Eng. Rudolf Lilljequist, would have met an almost insurmountable resistance from the authorities and the heirs had not the nephew of Alfred Nobel, Ludwig's son Emanuel Nobel, in February, 1898, declared that, although the death of Alfred Nobel had heavily shaken the financial ground of the Naphtha enterprises in Russia, he was willing to do his best to see that his uncle's will should be respected. The action of Emanuel Nobel on this occasion deserves to be remembered. Such a disregard as Alfred Nobel had shown of what was considered the rights of the heirs was, in fact, unheard of. Because of the extraordinarily good relations which always had prevailed within the family, Emanuel felt convinced that deeper motives had induced his uncle's decision. Therefore when the highest representative of the State claimed that Alfred Nobel had been "influenced by peace fanatics and particularly by women" and advised him to act in favor of the heir's rights, he responded:

"Your Majesty! It is not my intention to take any action through which members of my family in the future could be blamed by the most highly deserving scientists of the time for having deprived them of something which duly ought to be theirs."

Emanuel Nobel called the executors "solicitors of the soul." He participated in the preliminary discussions between them and the representatives of the Swedish Academy and the Karolinska Institute. A proposal was made on June 5, 1898, according to which the heirs would be allotted one-and-a-half years' income from the estate, provided they recognized the will and waived any further claims upon the estate. To this they agreed and thereby the estate was saved for the Nobel Foundation whose Articles were approved by His Majesty the King, Oscar II, on June 29, 1900. The following year, 1901, the first Nobel Prizes were awarded.[2]

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[2] The history of the Nobel Prizes in physics, chemistry, and medicine is intimately connected with the development of these branches of science after 1900. The history of the first 50 years in 1950 was summarized by the Nobel Foundation in the publication: "Nobel, the Man and his Prizes" (*3*).

In 1954, the Nobel Prize Winners in physics, chemistry, and medicine of the last 50 years were presented in separate volumes, the Laureates in physics by Heathcote (*4*), those in chemistry by Farber (*5*), and those in medicine by Stevenson (*6*).

A collection of the most representative writings of the Laureates in literature was edited by McClintock in 1948 (*7*).

German literature has lately revealed a lively interest in the Nobel Prizes.

Recently Schneider reviewed the prizes in physics "von Röntgen zu Einstein und von Planck zu Heisenberg" (*8*).

In three comprehensive volumes, "Via Triumphalis" (**1954**, 318 pp.) (*9*), "Via Gloriosa" (**1956**, 333 pp.) (*10*), and "Via Regia" (**1958**, 368 pp.) (*11*), Rudolf Erckmann has collected reviews presenting the Nobel Prize Laureates in chemistry, medicine, and physics and their work. The reviews were written by selected experts in the various fields. The three volumes constitute an exhaustive source of information about the men who have been honored by the Nobel awards, and about their scientific achievements as seen against their historical background.

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(1) Pauli, Hertha, "Alfred Nobel, Dynamite King, Architect of Peace," Nicholson & Watson, London; Brussels, **1947**, p. 323. Dutch edition: "Alfred Nobel, dynamitkoning, bouwmester van der Vrede," Haag, **1949**. Argentine edition: "Alfred Nobel—revdela dinamita—arquitecto de la paz," Ed. Poseidon, Buenos Aires, **1943**.

(2) Schück, J. H. E., and Sohlman, R., "Alfred Nobel och hans släkt." A Memorial Publication published for The Nobel Foundation by Almquist & Wiksell, Uppsala, Stockholm, **1926**, p. 325. German edition authorized by The Nobel Foundation, translated by Wolf Heinrich von der Mülbe, "Nobel, Dynamit-Petroleum-Pazifismus," Paul List Verlag, Leipzig, **1928**, p. 330. English edition authorized by The Nobel Foundation, translated from the German edition by Brian and Beatrix Lunn, "The Life of Alfred Nobel," London, **1929**. American edition, "Nobel, Dynamite and Peace," New York, **1930**.

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(4) de V. Heathcote, N., "Nobel Prize Winners in Physics, 1901–1950," Henry Schuman, New York, **1954**, p. 479.

(5) Farber, E., "Nobel Prize Winners in Chemistry 1901–1950," Henry Schuman, New York, **1954**, p. 219.

(6) Stevenson, Lloyd G., "Nobel Prize Winners in Medicine & Physiology, 1901–1950," Henry Schuman, New York, **1954**.

(7) McClintock, M., "The Nobel Prize Treasure. The Best from the World's Greatest Writers," Doubleday & Co., New York, **1948**, p. 612.

(8) Schneider, E., "Von Röntgen zu Einstein, von Planck zu Heisenberg," Gebr. Weiss Verlag, Berlin, München.

(9) Erckmann, R., "Via Triumphalis, Nobelpreisträger im Kampf gegen den Tod," W. Andermann, München, 1954, **1955**.

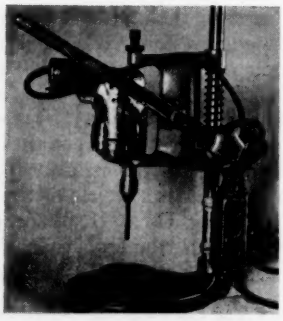
(10) Erckmann, R., "Via Gloriosa, Nobelpreisträger aus aller Welt dienen dem Leben," W. Andermann, München, **1956**.

(11) Erckmann, R., "Via Regia, Nobelpreisträger auf den Weg ins Atomzeitalter," W. Andermann, München, **1958**.

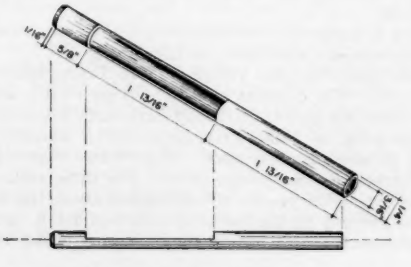
An Inexpensive Electric Cork Boring Machine

Robert Barnard, Montana State College, Bozeman

A low cost electric cork boring machine can be made from a 1/4-in. household-type drill and stand. The only modification to the drill stand is a small mercury switch installed on the handle so that when the handle is pulled down the drill will start automatically.



The details of a cork borer designed to bore cork and rubber stoppers to accommodate 6-mm tubing is shown in the diagram. The borer was machined out of mild steel. The opening in the side of the cutter makes this a self-cleaning device. Borers of various sizes can be made. A suggested modification is that the bevel of the cutter be reversed so that it is on the inside of the tube.



A Fast, Easy Method for the Preparation of Cross Hairs

Jerry W. Ellis

Kansas State College of Pittsburg

Due to the fragility of the cross hairs in telescopes and other instruments, they are sometimes broken or destroyed, and in many cases this renders the instrument useless. Repairing these broken hairs or making new ones presents somewhat of a problem.

An answer to the problem lies in a tube of plastic cement such as is used in the construction of model airplanes (Amco was used in this case) and a long pointed object such as a piece of stiff wire or a long thin nail. The hairs are made by putting a small amount of fresh glue on the pointed end of the object and quickly touching it to the frame and then again to the opposite side. Another one may be placed at right angles if desired, and this is probably the most difficult part of the entire operation. The hairs are literally generated from the glue, much like capillary tubes are pulled from glass tubing. The speed with which the operation is done is the critical factor. Since the glue solvent evaporates quickly and leaves a stiff cover over any exposed area of the glue, parts of this cover are pulled into the hair when it is generated. This results in a general non-uniformity of the hair diameter. If the operation is done too slowly, the hair will either not form, or will break before completion. When newly-formed hairs dry, they become taut and straight even if they were not taut when formed.

The technique required for production of suitable hairs may be acquired in a few minutes.

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Teaching Quantitative Analysis after Organic and Physical Chemistry

The conventional placement of quantitative analysis in the sophomore year has had the effect of restricting the instructor's scope, aside from the teaching of technique, to elementary and historical topics. Analytical chemistry as practiced by the professional analytical chemist today cannot be taught at the sophomore level. A student emerges from the typical first-year chemistry course ignorant of organic chemistry and either unacquainted with the chemical properties of all but a few elements or weak in his grasp of principles and calculations. This comment is not intended as a criticism of first-year chemistry courses; it is simply pointing out one of the realities of education. It explains why so frequently much of the time in sophomore courses in analytical chemistry is not spent in teaching analytical chemistry at all but is devoted to the very necessary task of improving the students' background in physical and inorganic chemistry to the point where he can function effectively. The undesirability of this situation, particularly from the standpoint of the professional analytical chemist, is evident.

Dissatisfaction with this and other characteristics of the traditional sequence led several years ago to a study within the MIT chemistry department to determine how most effectively to use the undergraduate chemistry major's time in acquiring a modern chemical education. The result was the development of a new curriculum which was first put into effect in the fall of 1957.[1] One of the most striking features of the plan was the placement of organic chemistry in the sophomore year and the removal of quantitative analysis to the second semester of the junior year. The present paper describes the general nature of the MIT course in quantitative analysis, for which organic and one semester of physical chemistry are prerequisites, and some of our experiences in giving it.

A basic tenet of undergraduate chemical instruction at MIT is that no one of the chemical sub-disciplines—analytical, inorganic, organic, and physical—should be subordinate to another. Consequently, the approach to analytical instruction is based on the following premises: (1) that analytical chemistry is important in its own right; (2) that analytical chemistry is a necessary part of the instruction of every chemist; (3) that what should be taught is the analytical chemistry in actual use today; and (4) that instruction in analytical chemistry, ideally, should be given by professional analytical chemists. In connection with the last point, it should be noted that in order to be taught really well, a subject must capture the imagination of the instructor as well as of the student. This cannot happen unless the instructor recognizes the subject as worthy of his best efforts and develops a feeling of identification with it. If a presentation is to be alive, the subject matter must be alive, and in this connection it is important that the teacher be associated with current research in the field.

The objectives of a quantitative course given at this level are necessarily somewhat different from the objectives of a quantitative course given in the sophomore year. It is reasonable to give and to expect the student to grasp a much broader and deeper view of the theory and principles of analytical methods than would otherwise be possible. The student's appreciation of the wide scope and great applicability of analytical methods is inevitably greater because by now he understands what chemistry *is*. At this level it is possible to realize that analytical chemistry is not just a collection of tests and determinations but comprises a great body of principles and methodology for the solution of those problems in

[1] HUME, D. N., J. CHEM. EDUC., **35**, 176 (1958).
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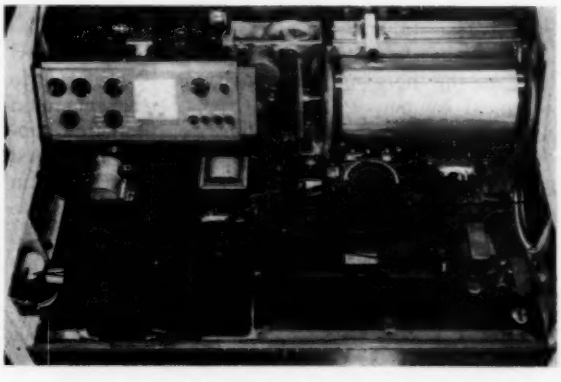
—The cover—



Appropriate both for featuring the second part of the Symposium on Educational Trends in Analytical Chemistry and the start of a series on Spectrophotometers in "Chemical Instrumentation" is this glimpse of what goes on in a B&L Spectronic 505.

The beam from source (A) is reflected, dispersed and collimated in the monochromator (BCDEFG). The beam is alternately chopped into the reference beam (IJM) and the sample beam (KLM) by the beam splitter (H). The beam recombiner (M) brings them back into coincidence on the photomultiplier (N). Intensities of light are translated into electrical pulses and ultimately recorded on the chart (upper right).

all branches of chemistry which involve physical and numerical measurements.

Enthusiasm for the theoretical aspects of the subject, however, must not be allowed to push the practical side into a secondary position. Analytical chemistry is a laboratory science. Of equal importance with theoretical understanding is the development of certain basic skills and good quantitative techniques. If this is to be done, the instructor must demonstrate to the student his own interest in the laboratory side of the subject. One must recognize the importance of instilling into every student a feeling of pride and satisfaction in a determination well done (and correctly calculated!).

The particular approach used at MIT is probably best illustrated by a description of what is done in the laboratory. Needless to say, the textbook situation constitutes a serious problem as no single text exists designed for a course at this level. The best compromise seems to be the use of two textbooks, one a standard introductory quantitative inorganic text[2] and another specializing in organic determinations, particularly by means of functional groups.[3] The inevitable gap between these two works must be bridged by generous use of mimeographed notes.

Laboratory Work in the MIT Course

In selecting experiments, every determination—no matter how firmly established in the traditional quantitative course—was re-examined and re-evaluated in terms of its actual pertinence to present-day chemistry. As a result, a surprising number of the traditional examples went by the board. It was felt that the introductory course should emphasize volumetric methods but also give some experience with the simpler instruments in universal use, such as the colorimeter and the *p*H meter. Gravimetric methods, in keeping with the relatively minor role which they play in contemporary analytical practice, were given little emphasis. Classical weighing techniques had already been taught the student in beginning physical chemistry laboratory, making it possible to employ single-pan automatic balances throughout.

The students are introduced to the laboratory work with acid-base reactions involving liquid unknowns, emphasis being upon the development of good technique in pipeting and titrating. Following unknown strong acid and sodium carbonate determinations, the determination of alcohol hydroxyl by acetylation is introduced. It is taken as a matter of course that functional group determinations should be interspersed freely among inorganic determinations. Nothing is to be gained by perpetuating the fallacy that common analytical methods are good only for inorganic substances. Oxidation-reduction methods are illustrated by the permanganimetric determinations of chromium and vanadium in a steel sample, nitro group determination by reduction with titanium trichloride, and phenolic group determination by bromination. A precipitation titration, the determination of halide with silver, is combined with the ion exchange separation of chloride and bromide, thereby providing a practical example of one of the most important of the modern separation processes. The great usefulness of EDTA in analysis is illustrated by the titration of calcium and magnesium. Both the practical and theoretical aspects of nonaqueous titrations are well brought out in the determination of an amine mixture by titration with perchloric acid in glacial acetic acid. Of the many gravimetric determinations available, the estimation of nickel with dimethyl glyoxime (fritted glass crucible) and of sulfate by ignition of barium sulfate were thought to be the most instructive.

While it is felt that instrumental analysis belongs properly in a separate semester, certain of the simpler instruments are so universally found in modern laboratories that an introduction to their use belongs in the beginning analytical course. Colorimetric analysis is represented by the determination of manganese in steel, and the use of the *p*H meter by the titration of a weak acid-strong acid mixture. The flame photometer, applied to the determination of alkali metals in simple and complex mixtures, serves also to illustrate internal standard and standard addition methods.

The above series of determinations, performed by all students, is designed to occupy approximately half the semester. The rest of the term is devoted to the performance of several special determinations, chosen by the individual student, and a project of a research nature. As would be expected, these special projects stimulate a great deal of response on the part of the student.

The lecture portion of the class places a considerable emphasis on basic principles and the theory underlying analytical methods. Theory at this level can be treated adequately, as there is no need to avoid the use of structural principles, organic reactions, or simple thermodynamic and kinetic equations. For each type of analysis, basic theory, practical considerations involved in actual use, and a survey of applications are discussed. Organic functional group analysis is given a prominent position and the various separation methods—chromatography, ion exchange, precipitation, solvent extraction, etc., are both treated individually and intercompared. Every effort is made to give the student an appreciation of the applicability of analytical methodology to his own problems in all branches of chemistry and a feel for the analytical approach to their solution.

The initial response to this type of teaching has been a favorable one. The students are stimulated by the material and respond with an interest never seen in the sophomore laboratory. It will be some time before the ideal balance of topics is found and quite some time before the textbook situation ceases to be a problem. The experience to date, however, indicates that the result is well worth the effort, and we are convinced that the present experiment is a move in the right direction.

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[2] Hamilton, L. F., and Simpson, S. G., "Quantitative Chemical Analysis," 11th edition, The Macmillan Co., New York, 1958.

[3] Fritz, J. S., and Hammond, G. S., "Quantitative Organic Analysis," John Wiley & Sons, New York, 1957.

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and **D. D. DeFord**
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Evanston, Illinois

Analytical Chemistry between Organic and Physical Chemistry

During the past six years the following three quarters of undergraduate analytical chemistry have been offered at Northwestern University: (1) Introductory Quantitative Analysis, which includes the fundamental principles requisite to an understanding of volumetric and gravimetric methods, (2) Instrumental Analysis, which is devoted primarily to spectral and electroanalytical methods, and (3) Separations, which includes extraction, volatilization, chromatography (partition, adsorption, and ion-exchange) and precipitation.

The normal sequence of courses taken by the undergraduate chemistry major is general chemistry (including qualitative analysis) in the freshman year, organic chemistry in the sophomore year, the above sequence of analytical chemistry in the junior year,[1] and physical chemistry in the senior year. In addition, a quarter of advanced inorganic chemistry, which is taken in either the junior or senior year, is required for majors. Students maintaining a B average or better normally include 8–12 quarter hours of honors research and one or two advanced courses in their senior-year program.

Adequate preparation in mathematics and physics is an essential prerequisite for an effective course in modern analysis. At Northwestern University, the requirements of the college of liberal arts make it extremely difficult for a student to complete this preparation in the freshman year, thus precluding the possibility of offering the complete analytical sequence in the sophomore year. Since introductory organic chemistry is less dependent on previous preparation of this type, it may be taught as effectively in the sophomore year as in the junior year. Furthermore, the placement of organic chemistry in the sophomore year permits a discussion of all types of analysis, both organic and inorganic, thus obviating the necessity for a separate course in organic analysis.

It may be argued that physical chemistry would be a desirable prerequisite for the second and third quarters of the analytical sequence, and it must be admitted that these courses could be taught somewhat more easily if the student had prior training in physical chemistry. We have experienced no problems in introducing the necessary physicochemical concepts in the analytical course, and we believe that the disadvantages in teaching the analytical courses before physical chemistry are slight. On the other hand, prior courses in analytical chemistry offer a considerable advantage in the teaching of physical chemistry, and we believe that these advantages are at least as great as those which might be realized by the reverse sequence.

[1] The first quarter of analytical chemistry serves both as an introductory course for the chemistry major and as a service course for premedical and engineering students. As such it can be taken in the sophomore year. Organic chemistry is a prerequisite for the second and third quarters; when all three quarters are taken, it is recommended that they be taken in sequence.

Presented as part of the Symposium on Educational Trends in Analytical Chemistry, sponsored jointly by the Divisions of Analytical Chemistry and Chemical Education, at the 136th Meeting of the American Chemical Society, Atlantic City, N. J., September, 1959.

Course Content

The following is a brief description of the course content of the sequences of courses outlined above. In the first quarter the various methods by which chemical reactions are utilized in the measurement of concentration, the types of reactions and specific reagents most commonly used in volumetric and gravimetric procedures, sources of errors and the statistical treatment of experimental data, solution equilibria in general, and finally, titration curves, chemical indicators, and titration errors are covered. In order to discuss oxidation-reduction titrations, it is necessary to introduce the concept of electrode potential in the course although a detailed coverage is reserved for the second quarter.

Because spectroscopic and electroanalytical methods are the most widely used in practical analysis, the primary emphasis in the second quarter is on these methods. Several other methods are very briefly discussed in order to give the student some appreciation of the broad scope of instrumental techniques. Here again the emphasis is on the underlying principles of the methods.

In presenting the general topic of spectroscopic methods, considerable time is devoted to the origin of spectra, the types of energy transitions which occur in the different regions of the spectrum, the quantitative laws that govern the absorption of radiation, and the factors that govern the intensity of emitted radiation. The discussions of emission (flame, arc, spark, and fluorescence) and absorption methods (X-ray, ultraviolet, visible, and infrared) are then devoted primarily to practical considerations. All of the electroanalytical methods, with the exception of conductivity, are presented with the aid of current-potential curves. After a consideration of the general problem of mass transfer and a further discussion of electrode potentials, the wave equations for several types of reversible electrode processes are derived. The characteristics of irrevers-

ible waves and kinetic waves are discussed qualitatively but are not treated in detail. These current-potential curves then serve as the basis for a discussion of both the theoretical and practical aspects of the various electro-analytical methods such as polarography and voltammetry, electroseparations, coulometric analysis, and the various amperometric and potentiometric titration methods.

The separations course is devoted primarily to a discussion of extraction, chromatography, and precipitation, but other separations methods are discussed briefly. The case of a simple single-contact extraction with constant partition coefficient is introduced first and methods of adjusting the partition coefficient (i.e., *p*H, complexation, salt concentration, solvent, etc.) are discussed. This simple case is then expanded to successive extractions and finally to countercurrent methods. In the latter, the equations for concentration versus tube number are developed and band spreading and resolution are discussed. The theory of the different classes of partition chromatography (gas-liquid, liquid-liquid, and ion-exchange) can now be treated simply by introducing the concept of the theoretical plate and applying the theory developed for countercurrent methods. Finally the student is introduced to the phenomenon of asymmetic bands which arise in adsorption chromatography (gas-liquid and liquid-solid) due to the non-linear adsorption isotherms. Precipitation methods are treated separately; factors influencing solubility, limitations of equilibrium calculations, properties of precipitates, coprecipitation, and precipitation from homogeneous solution are covered.

Laboratory Work

Six hours of laboratory per week are available for each course. In the introductory course, the students perform the following seven analyses: (1) gravimetric determination of chloride as silver chloride, (2) Volhard determination of chloride, (3) titration of acetic acid unknown with sodium hydroxide (involves standardization of sodium hydroxide with potassium acid phthlate), (4) determination of molecular weight and pK_a of an organic acid by a titration employing a *p*H meter, (5) determination of iron in an iron ore by titration with potassium dichromate, (6) determination of copper in an ore iodometrically (involves standardization of sodium thiosulfate with potassium dichromate), and (7) the determination of calcium and magnesium in limestone by titration with ethylenediamine tetraacetic acid.

The laboratory part of the second quarter has been varied considerably over the past several years but generally includes experiments such as: quantitative polarography with the DME, determination of formula and stability constant of a complex ion by polarography, controlled potential and constant current coulometric analyses, electro-gravimetry, the detemination of current-potential curves with RPE at various stages of a titration, and the use of these curves in selecting appropriate conditions for a variety of potentiometric and amperometric end-point detection methods, conductometric titrations, and several colorimetric and spectrophotometric determinations. Three-hour demonstration experiments are carried out with infrared spectrophotometers, recording ultraviolet spectrophotometers, and automatic titrators since these instruments are not available for individual student use in the course.

The laboratory work in the third quarter normally consists of only two separate experiments. The first of these involves the determination of one or more constituents in a complex sample. A different sample is assigned to each student. The constituents determined may be present in either macro or trace amounts and may be either organic or inorganic in nature. Normally the samples used preclude the use of very simple analytical methods, and preliminary separations to remove interferences are usually necessary. No directions for carrying out the analysis are provided; rather, the student is required to carry out a literature search to discover suitable methods. After the proposed methods have been approved by the instructor, the student sets up and calibrates the required equipment and carries out the analysis, usually by two different methods. The accuracy required of the student depends on the particular sample and is specified in advance; normally an accuracy comparable to that which can be achieved by the best available methods is specified.

For the second experiment in the third quarter the student is required to check-out a separation method described in the recent periodical literature. The work described in the assigned paper is repeated, and a detailed report is submitted. Students are encouraged to suggest and to study possible modifications, improvements, and extensions of the method. Again different papers are assigned to each student, and the papers are selected so that at least one student is studying each of the major separation techniques. The work load in the laboratory is light enough that each student has time to observe the work that his colleagues are doing and to gain some familiarity with all of the methods being studied.

All students, and particularly the better students, respond with tremendous enthusiasm and interest when they are required to rely on their own initiative, as is the case in the third quarter laboratory, and the learning process is greatly facilitated. Despite the fact that the student gains first-hand experience with only a few methods, we are convinced that he learns far more than he does from a series of cookbook experiments designed to give some experience with all methods.

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Graduate Education in Analytical Chemistry

Graduate students in chemistry continue to be well provided with both classical and modern analytical courses. Usually, wide choice is possible. The problems of graduate education in analytical chemistry lie more at the research level and beyond. These are summarized briefly.

Fundamental versus Applied Training

It is the custom of industry in the United States when it searches for new chemical personnel to ask for an analytical, inorganic, organic, or physical chemist. We do not quarrel with industry's need for classification and specialization of labor. We *are* concerned when an industry prefers for employment an analytical chemist who has spent his time in graduate school emphasizing techniques and carrying out a trial-and-error type of thesis research in preference to one who not only knows techniques but has prepared himself in fundamental knowledge of chemistry, has developed his ability to use it, and has chosen a thesis subject because of its challenge in ideas and probable contribution to fundamental knowledge. A Ph.D. who has not had the experience in his research of coming to grips with fundamental ideas and having to find his way through has missed not only one of the finest experiences but also the real purpose of the Ph.D. program.

There is a philosophy of analytical chemistry which exceeds the everyday repetition of routine analysis. It leads to the imaginative development of ideas. The significant developments in analytical chemistry have frequently been made by men of broad, fundamental training with curiosity about the frontiers of chemical knowledge. We suggest that we who bear the label "Analytical Chemist" in the universities continue to emphasize as our major objective the study of fundamental ideas.

Influence of Supports on Research in Universities

Two statements were recently made by university officials, not to be identified. One said that *he* classified all university research into two categories, *useful* research and *hobby* research. By *hobby* research he meant those ideas that appear intellectually interesting but do not have obvious practical objectives. He proposed that financial support be restricted to what he called useful research. The second official said that what we need today is more "doers" and less "thinkers." Both men have a lot to say about the assignment of research funds in their universities. These examples indicate the need for educating the less than professional scientist in the meaning, necessity, and value of fundamental, long-range research.

Much university research continues to be supported by off-campus sources. President Stokes of Queen's College said recently, "[T]he major Departments of Physics in this country would be shadows of their present selves if the support of national agencies were withdrawn."[1] Similar outside support is now accepted as an integral part of the graduate program in chemistry in spite of certain secondary effects on the universities' traditional plan of support of graduate work.

These secondary effects include: (1) Support of graduate students on a 12-month basis in contrast to the 9 or 10 month support for the teaching assistant. (2) Larger monthly incomes for graduate students than the university pays them as teaching assistants. (3) Greater attraction for the supported research problem if it can also be counted toward the thesis. (4) Transfer of the better teaching assistants to supported research assistantships which hurts the quality of undergraduate teaching and the attraction of the undergraduate major. (5) The dependence of the professor who does not have a supported program upon the intellectual attractiveness of his research to offset the economic disadvantage of working with him. We must give credit to those professors who continue to attract good graduate students in spite of the economic differential. (6) The unnatural direction of a professor's research toward sources of support. How much valuable hobby or personal interest research has been neglected in the competition with supported research?

In 1958, one third of the papers appearing in *Analytical Chemistry* from universities acknowledged financial support from outside agencies. One asks what these authors might have done without this support. Here we see the direction of research being influenced subtly by forces outside the university.

Many national agencies attempt to award support without primary concern for the obvious practical usefulness of the results. However, much research in universities has industrial support, and it is only reasonable for the industry to expect some immediate, practical results. If the university allows graduate students to use the research done in such projects for thesis purposes and the student is literally paid for doing a thesis, it becomes clearly a prostitution of purpose by the university. The professor in charge of supported research has the responsibility to deal with these serious by-products of support.

Presented as part of the Symposium on Educational Trends in Analytical Chemistry, sponsored jointly by the Divisions of Analytical Chemistry and Chemical Education, at the 136th Meeting of the American Chemical Society, Atlantic City, N. J., September, 1959.

[1] STOKES, HAROLD W., "The American College President," Harper and Brothers, N. Y., 1959, p. 7.

The Challenge of Organic Analytical Chemistry

Traditionally, analytical courses in the universities have dealt with inorganic systems. Inorganic systems were thought to be more understandable and better defined. Organic combustion elemental analysis did begin early but like organic qualitative analysis was usually included in organic chemistry.

Abstracts on organic analysis are rapidly increasing in number and in proportion in Section 7 of *Chemical Abstracts*. It has been suggested by several organic chemists that Section 7 be divided into two parts, Inorganic and Organic, in order to save the time of the increasing number of readers interested only in organic analysis.

Development of non-aqueous titration systems, polarography of organic compounds, infrared spectroscopic identification, identification based upon kinetic studies, C^{14} labeling, mass spectrometry, nuclear magnetic resonance, and chromatography show the recent great progress in organic analysis. The teaching of analytical chemistry in the universities has the challenge before it of how to include a reasonable amount of organic analysis and retain the theory now considered important in inorganic analysis.

Analytical Chemistry for Non-Specialists

A survey over several years of the non-analytical graduate students in this department representing all of the states of the Union indicated that nearly all expected, if they went into industry, that their analytical needs would be supplied by company analytical services. This impression from professors and employment interviews seemed to be the reason for the non-analytical graduate student not selecting advanced courses in analytical chemistry.

Industrial friends state that this is an unwise point of view for the graduate student specializing in other than analytical chemistry; most industrial research does involve analysis, and the research chemist must bear the responsibility if not perform the labor in many cases. The universities could, I believe, benefit from encouragement by industry for the inclusion of some analytical chemistry in the program of every graduate student.

The same survey indicated that over 80 per cent of our graduate students received their undergraduate instruction in analytical chemistry from professors whose major interest and training were in the order: organic, physical, inorganic, and analytical. Many of the courses in analytical had been taught by the method of the instructor's handing the student a sample and a textbook and telling him to return when he was finished. One professor, in discussing the popularity of a certain textbook in quantitative analysis, thought it exists because its use requires a minimum of the professor's time. Obviously we need more analytical majors teaching in the undergraduate colleges if we are to correct these difficulties at the graduate level, difficulties which seem to have an origin in undergraduate work.

Originality of Research in a System of Classified Reports

Three times in our experience, papers reporting work very similar to ours have appeared after the announcement of and before the publication of our paper. In each case the paper came from a laboratory doing classified work. The submission dates on all three papers clearly indicated their receipt after the announcement dates of our papers. The work had apparently been done previously and reports stored in the files. This problem relates to the government's secrecy problem. One's only satisfaction is that someone else thought the problem was important too. The universities need to develop a method for establishing the originality of research proposals in areas where classified work occurs.

Simultaneous duplication of research also is occurring with increasing frequency. In an industrial laboratory, this may not be so important. In universities where so much emphasis is placed upon originality at the time the thesis is completed, it can be devastating to the graduate student suddenly to find his research in the latest copy of a journal. If the similarity is not too great, the student is fortunate. In any case there seems no obvious solution for this serious problem.

Storage and Retrieval of Information

By this, we mean searching, selecting, co-ordinating, and translating already published information. Much time is spent on literature searches. In one case, a student spent over 9 months searching and finally discovered an obscure paper that covered the problem he hoped to study. An expanded abstracts system does not seem to be the answer. Abstract indexes already take much library space as well as the individual's time in searching. Competition for the use of the indexes is also a serious problem. Much use rapidly wears out the pages and binding. Whatever new system we develop for storage and retrieval of information must make primary allowance for completeness and for minimum search time. The magnitude of chemical literature has now become so great and the degree of specialization so advanced that it suggests we might recognize some of the subfields as independent areas and ask them to develop and support their own journals and abstracts.

Literature exchange devices in analytical chemistry are also needed. MIT has recently arranged to exchange 500 text and reference books in science and engineering for 500 of those published in Russia. How can we in analytical chemistry benefit from such an exchange program?

Analytical chemistry needs more publication space. Editorial policies are under severe financial pressure and pressure from an increasing number of papers submitted. The establishment of new journals is hardly the answer since they must derive their support from the same limited sources of funds as do existing journals. Publication in foreign countries under conditions of cheaper labor is probably not an acceptable solution. Perhaps a completely new device for publication, some departure from the printed paper page, may be needed in order to resolve problems of space and cost.

A final suggestion is that the *Journal of the American Chemical Society* recognize the accomplishments of analytical chemistry by identifying papers in this field. Graduate students think it peculiar that analytical

chemistry was not for many years identified as such in the *Journal of the American Chemical Society*, and this concern is reflected in their opinions of the analytical profession. The argument that analytical has its own journal and therefore does not need the *Journal of the American Chemical Society* is not consistent since organic and physical and inorganic also have their own journals as well as the *Journal of the American Chemical Society*. The stature of analytical chemistry in 1959 makes it a reasonable and irresistible request that analytical chemistry papers be placed in an identified section of the *Journal of the American Chemical Society*.

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Analytical Chemistry at Harvey Mudd College

Three years ago during a symposium on "New Ideas in the Four-Year Curriculum" sponsored by the Division of Chemical Education, the chairman of our department pointed out that one of the most obvious "new ideas" in the proposed chemistry curriculum at Harvey Mudd College was the redistribution of the classical analytical course among courses offered during the entire four years. Harvey Mudd College has been in operation for three years now under the curriculum blueprint outlined at that time.[1] The purpose of this paper is to review what we have done with analytical topics in our freshman, sophomore, and junior programs and to indicate our present thinking about the senior program.

First of all, however, it seems reasonable to include a brief background of the organization of Harvey Mudd College in order to establish for the reader the almost unique position in which we find ourselves. Harvey Mudd is a college of physical science and engineering, the fifth and newest of the Associated Colleges at Claremont.[2] The college was established in 1955 and in 1957 a faculty of 7 welcomed the initial class of 48 freshmen. By the fall of 1959, the college included a student body of 156 and a faculty of 27, 5 of whom are chemists. During his freshman and sophomore years every student in the college takes a common program of two years of chemistry, physics, mathematics, and humanities, one and one-half years of engineering problems, and one year of social science. As he enters the junior year the student begins to concentrate his scientific efforts in one of the four fields in which we offer a degree—chemistry, engineering science, mathematics, or physics. Before graduation he must also complete an additonal two years of course work in both the humanities and the social sciences. It is interesting to note that of our junior class of 35 in the 1959–60 academic year, 10 elected to major in chemistry.

The chemistry program at present includes a year of general chemistry with emphasis on both structural concepts and the nature of dynamic equilibrium, and an intensive course in physical chemistry during the sophomore year which emphasizes thermodynamics, kinetics, molecular structure, and the solid state. As these two courses are required of every student in the college, they serve as the chemical background for those planning to major in the other three disciplines as well as for those continuing in chemistry. Because of this unique situation, the chemistry department is actively exploring the feasibility of offering a more completely unified two-year sequence in chemistry which will certainly include a large proportion of the topics we are covering at present and which will lean very heavily on chemical principles but will be more specifically designed for our environment.

As a junior, the chemistry major takes both a year course in organic chemistry and a year of inorganic chemistry. These courses are based on the foundations of physical chemistry developed during the sophomore year, thus permitting the organic course to give more emphasis to mechanisms and the inorganic course to thermodynamics than is possible in most courses at this level. The focus of the senior year lies in a laboratory research problem which is complemented by a biweekly seminar in which contemporary research is discussed by students, faculty, and visiting scientists. In addition, the chemistry major is required to take two additional one-semester courses, one in analytical chemistry and one in either advanced organic or advanced physical chemistry.

On paper, then, it appears as though we at Harvey Mudd College are trying to compress analytical chemistry into a one-semester course in the senior year. As that course will inevitably treat mainly instrumental methods of analysis, it is reasonable of the reader to ask what we have done with the more conventional and classical analytical measurements and theory.

Redistribution of Experience in Analytical Chemistry

From the beginning, in the freshman laboratory we introduce the student to quantitative measurements and techniques. Weighings are made on a one-tenth

[1] CAMPBELL, J. A., J. CHEM. EDUC., **35**, 172 (1958).
[2] SMITH, R. N., J. CHEM. EDUC., **33**, 642 (1956).

Based on a paper presented as part of the Symposium on Educational Trends in Analytical Chemistry, sponsored jointly by the Divisions of Analytical Chemistry and Chemical Education, at the 136th meeting of the American Chemical Society, Atlantic City, N. J., September, 1959.

milligram analytical balance, and gravimetric experiments include the determination of the combining ratio of silver to chlorine, the equivalent weight of a metal, and the formula of a hydrate. Volumetric experiments include both acid-base and oxidation-reduction titrations in which an increasing degree of accuracy and precision is required as the year progresses. During the past year we have also had the student determine the chemical formula of an insoluble salt or of a colored complex ion by the method of Job, and then determine an equilibrium constant for the system by visual colorimetry. Some elected to use an acid-base titration as a means of determining the ionization constant of a weak acid or base. Since there are a great many more experiments available to the student in the freshman laboratory than he can possibly do, it is for him to decide which experiments will be of most interest and value to him. He is not to repeat any experiments which he has done in high school or for which he can predict the results. Thus he is encouraged to do quantitative experiments rather than purely qualitative ones. We at Harvey Mudd College enthusiastically concur with Swift[3] on the desirability of introducing more quantitative chemistry into the freshman laboratory.

The freshman laboratory also includes the eight-bottle experiment which Campbell discussed three years ago[1] in which, during one of the first laboratory periods of the year, the student is confronted with three bottles labeled "reagents," four labeled "knowns," and one labeled "unknown." It is his task to learn to use the reagents to identify each known singly or in any possible combination and then to identify his unknown which may contain from one to four of the knowns. We find this to be a highly successful experiment in that it requires the student to organize an attack on a problem, to observe carefully the results of his own planned experiments, and then to draw meaningful conclusions from the results. It sets the tone for the remainder of the laboratory work of the course. During twelve weeks of qualitative analysis in the second semester the student is encouraged to develop his own scheme of analysis or spot-test methods for the detection of anions and cations in a variety of unknowns each of which may contain only a limited number of constituents chosen from a known list.

In the sophomore course in physical chemistry the student continues the development of his analytical experience, here primarily as a means of obtaining the requisite physical data. Laboratory experiments have included the following: From the results of distribution experiments of benzoic acid between water and an organic solvent in which the aqueous phase was analyzed for benzoic acid the student was asked to determine the dimerization constant of benzoic acid in the organic phase as well as the distribution constant of benzoic acid between the two phases. The rate of oxidation of formate by silver ion was followed by a back titration of the amount of silver remaining at various times using an adsorption indicator. The students have also determined the indicator constant of methyl red by a combination of spectrophotometric and *p*H measurements. Beginning with this course and from then on weighings are made with a single-pan, semiautomatic balance.

[3] SWIFT, E. H., J. CHEM. EDUC., **35**, 248 (1958).

Analytical Chemistry in the Inorganic Chemistry Course

The junior year inorganic chemistry course given for the first time in 1959–60 is a synthesis of intermediate inorganic chemistry, analytical chemistry, and electrochemistry. The laboratory work of the course consists of some rather classical analytical experiments, some inorganic preparations followed by analysis, some simple electroanalytical experiments, and some physicochemical experiments in which analysis is the means of obtaining the desired physical data. Each student is given a great deal of freedom in selecting his experiments within a given area under consideration.

The first semester laboratory was organized in general this first time around the topics in Swift, "Introductory Quantitative Analysis,"[4] and included volumetric precipitation, oxidation-reduction, acid-base, and gravimetric methods.

Each student first calibrated a buret and pipet; these are to remain his during his stay at Harvey Mudd College. We feel that it is important for the student to gain some feeling for buoyancy effects and for the effect of temperature on the volume of solutions and glassware. Eventually when the freshman laboratory is housed in more permanent and more spacious facilities we intend to have each freshman calibrate a buret which will remain his as long as he is enrolled in any chemistry course in the college.

Next the student did a classical determination of chloride by the Mohr method. This was included primarily in order to test the analytical techniques which he brought with him into the course. It was very encouraging to note that 8 of the 10 students reported values which were within $\pm 0.2\%$ of the recorded values for this analysis. This was followed by an experiment patterned after those suggested by Ramette[5] in which the students as a team estimated the thermodynamic solubility-product constant of mercury(I) sulfate. The class was divided into two groups of five students each. Each student determined the solubility of mercury(I) sulfate in a solution containing a different sulfate ion concentration, but within each group the ionic strength was the same. Directions were minimal and after an introductory lecture on activity coefficients and ionic strength the student prepared and equilibrated his own system and then analyzed the solution for the mercury(I) ion concentration by means of a Volhard titration, after first oxidizing the mercury to the dipositive state. From his data each student calculated a concentration solubility-product constant, and by using those obtained by the whole class he estimated a thermodynamic solubility-product constant.

Oxidation-reduction experiments were chosen from a list which included the preparation and analysis of iron(II) diammonium sulfate, copper(I) chloride, chromium(II) acetate, and uranium(IV) oxalate, and classical determinations such as the iron, copper, antimony, or arsenic in an ore. A Jones reductor and a wide variety of oxidizing and reducing agents were used. In the acid-base topic the student prepared and standardized solutions of sodium hydroxide and

[4] SWIFT, E. H., "Introductory Quantitative Analysis," Prentice-Hall, Inc., New York, 1950.

[5] RAMETTE, R. W., J. CHEM. EDUC., **33**, 610 (1956).

hydrochloric acid. These were then used in experiments chosen from among the preparation and purification of sulfamic acid for use as an alkalimetric standard, the preparation and analysis of magnesium nitride, a Kjeldahl determination of nitrogen, the analysis of soda ash, the analysis of a phosphate mixture, and the determination of the equivalent weight and equilibrium constant of a weak acid or base. Each student had the use of a *p*H meter for any of the last three experiments of this group. Finally, one gravimetric experiment was selected, either the determination of chloride or of sulfate, using respectively sintered glass or porous porcelain as the filtering medium. From the large group of optional experiments each student did at least one preparative experiment and most did two.

The laboratory work of the second semester began with the determination of the solubility-product constant of calcium sulfate and the dissociation constant of the hydrogensulfate ion. This was another experiment similar to the mercury(I) sulfate experiment of the first term, but with notable exceptions. The students were given no directions for the experiment other than some lectures on the chemistry of ethylenediaminetetraacetic acid (EDTA) which was used as the titrant for calcium in the experiment, and a formal report in the style of a journal article was required.

The largest single topic of the second semester was that of electrochemistry, in which the student performed experiments in the areas of electrodeposition at constant current, coulometry, conductivity, and potentiometry. Electrodeposition experiments included the determination of copper in an ore, the determination of copper and lead in a brass, or the analysis of a copper-nickel solution. Optional coulometric experiments included the determination of arsenic(III) by titration with electrolytically-generated iodine or bromine, or the determination of hydrogen ion with electrolytically-generated hydroxyl ion, using either a visual or a potentiometric end point. Conductivity included the measurement of the conductance of solutions of strong and of weak electrolytes including the determination of the ionization constant of a weak acid or base; and conductimetric titrations such as acid-base, precipitimetric, or ion combination. Potentiometry included the determination of the electromotive force of cells both with and without liquid junction; potentiometric titrations in aqueous solution, either acid-base using a quinhydrone electrode, oxidation-reduction, or precipitimetric; or acid-base potentiometric titrations in non-aqueous solvents such as glacial acetic acid or acetonitrile. Two experiments were required of the student in both the conductivity and potentiometry areas, one to illustrate the theory of the method and the second to illustrate an analytical application. The student was encouraged to make two different types of potentiometric and conductimetric titrations. A cation exchange resin was used whenever possible to prepare the solution to be analyzed by one of the electrochemical methods.

The remainder of the second semester consisted of the preparation and analysis of a complex coordination compound of a metal such as cobalt or chromium, and the analysis of an alloy or ore. For this last experiment the student first had to prepare a solution of the unknown, then make a qualitative analysis, next devise a separation scheme for two or three of the major constituents, and finally make a quantitative estimation of these constituents by any technique he had developed by that time.

The lecture part of the course was designed to parallel the general areas suggested by the laboratory outline, but it also included a survey of systematic inorganic chemistry as well as topics such as bonding and reaction mechanisms.

Other Courses

The organic course also offered for the first time in 1959–60 included some qualitative organic analysis, functional group analysis, and an introduction to the scope of light-absorption analysis.

The only course in our curriculum entitled "Analytical Chemistry" will be offered for the first time in the 1960–61 academic year. Since the chemistry faculty have been actively engaged in planning and developing the new junior courses and in evaluating and revising the freshman and physical chemistry programs, we have not been able to give much time to the detailed planning of this senior year course. As it is conceived at the present time, however, the course will be primarily concerned with instrumental methods of analysis. We intend to cover topics in electrochemistry such as polarography, amperometry, and other electrometric end-point techniques that were not treated in the inorganic course; light absorption and emission analysis including colorimetry, visible, ultraviolet, and infrared spectrophotometry, and flame photometry; and various aspects of chromatography.

It is still somewhat early to evaluate the results of our program in analytical chemistry. Our founding class has just finished a major portion of its analytical experience in the junior year inorganic course but has yet to complete the senior year analytical course. I can say, however, that our physical chemists do not feel that the students have been handicapped in their laboratory work in physical chemistry by their limited amount of training in analytical techniques. The junior-year inorganic course was well received by the students, especially the laboratory part. They like the broad selection of experiments available, and most enjoyed making precise analytical measurements after a year of physical chemistry in which relatively large errors were the general rule. The interspersion and combination of preparative and physicochemical experiments with the analytical seemed to heighten interest, although there were some who did complain of the many standard solutions they had to prepare and of the innumerable times they had to use a buret. In general, I have been extremely gratified by the interest of our first chemistry majors in their analytical work, and I have been impressed with the mature attitude they have consistently shown in their approach to the laboratory problems.

Editor's note

A final paper from this symposium, "Research-Oriented Experiments in Instrumental Analysis," by D. T. Sawyer (California) and C. N. Reilley (North Carolina) will appear in the August issue.

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A Realistic Introduction to Solution Equilibria

I cannot honestly claim that the use of the approach to be described in this paper has yet been widespread enough to be accurately classified as a *trend*. However, the chairman agreed that the symposium could legitimately include papers which present ideas of an experimental nature. Actually, the only fundamental trend of which I am aware is the increasing dissatisfaction with the traditional teaching of analytical chemistry. There is a growing tendency to deemphasize the subject of analytical chemistry *as such* in the curriculum, and unhappily there are good schools which no longer offer actual courses in this subject.

We all should be interested in the problems of making analytical courses more stimulating while at the same time retaining much of the same general subject matter. Previous papers have expressed deep concern over the role of the laboratory (*1*, *2*), where we have long sold our subject short. At this time I should like to place emphasis upon the material covered in the lecture course, with reference to a major phase of analytical chemistry: aqueous solution equilibria. The object of the proposed approach is not merely to correct some of the factual errors and superficialities which exist in the usual treatment, but especially to put into practice a philosophy which is quite different.

We certainly realize that a sound understanding of solution equilibria is both necessary and fundamental to an appreciation of analytical processes in general. In most schools, the subject of equilibrium is taught in courses in qualitative and quantitative analysis, by analytical chemists. The subject is classified accurately as part of analytical chemistry as well as part of physical chemistry (whatever *that* is!).

Basically, the prevalent approach continues to be the *use* of equilibrium principles to explain the methods of analysis. Judging from the treatment presented in many of the textbooks of analytical chemistry, the material is presented as a series of cut-and-dried facts and principles. I am little aware of any tendency to show the field of solution equilibria as living and changing, with many major frontiers of knowledge and countless minor ones, *most of which are within reach of the serious undergraduate student*. The analytical processes have been the backbone of the courses, and the subject of aqueous equilibria has been denied its sparkle as an intellectually satisfying area of research. I do not say that we should have *no* courses in which the analytical processes are indeed the chief subject—my own course in quantitative analysis largely follows this path. But the subject of equilibrium is so vital in so many areas of chemistry that it fully deserves a higher status in the curriculum. Research in equilibrium is active and widespread and is very largely an analytical problem, for without successful analyses no equilibrium system can be solved. It is not necessary but it is certainly appropriate that analytical chemists should be the ones responsible for this subject in the curriculum, and it is also appropriate that we should adopt a more responsible attitude toward the quality of the material presented to the students.

At Carleton College we had long offered a course in qualitative analysis along traditional lines. Because of the attitudes expressed in this paper the course has evolved into a new approach. The qualitative laboratory work has been discarded, with the contention that it is extremely wasteful of the student's time. This is without reference to the large amount of valuable descriptive inorganic chemistry, which is the chief justification for teaching qualitative analysis in the twentieth century. Rather, the waste is in the countless repetitive operations which are carried out *à la recipe* in spite of any conscientious determination on the part of the instructor. Also, the laboratory work of qualitative analysis held a whip hand over much of the lecture material, and it was necessary to spend a good deal of time on the scheme itself. The absence of such a laboratory program permits freedom to treat aqueous equilibria from a research-oriented view. The new approach has two major premises: (1) that it is much more valuable *and* interesting to study the methods of discovery than merely to apply someone else's mysteriously determined equilibrium constants to weakly practical problems, and (2) that it is important to treat any worthwhile subject with as much depth as possible *during the first exposure*.

This paper will be a brief sketch of the new course. I expect the course to evolve and improve rapidly with respect to organization and specific detail, and although the basic philosophy will not change, it is premature at this time to give a thorough outline. An accompanying paper[1] will present an examination of an abridged version of a selected topic as covered in the course, comprising discussion and problems which are handed out to the students. The purpose of this second paper is to illustrate the *type* of approach which is proposed.

To put the new course in curricular perspective a word is necessary about our new curriculum. Following the lead of Wabash College (*3*) we are cooperating with the physics department to offer a one-year course in chemistry-physics which serves as the only introductory course in the two departments.

Presented as part of the Symposium on Educational Trends in Analytical Chemistry, sponsored jointly by the Divisions of Analytical Chemistry and Chemical Education, at the 136th Meeting of the American Chemical Society, Atlantic City, N. J., September, 1959.

This paper is concerned with the next chemistry course, in the first semester of the sophomore year, entitled "Equilibrium." This is followed by a course in "Analytical Chemistry," in which the principles of gravimetric, titrimetric, spectrophotometric, and potentiometric methods are studied in the light of the equilibrium principles covered in the first course. The equilibrium course uses certain analytical methods in the laboratory work as an aid in obtaining data for equilibrium calculations; so the two courses interlock.

In the junior year the chemistry major will take organic chemistry and structural inorganic chemistry (elective) in the first semester, and organic chemistry and thermodynamics in the second semester. In the senior year he will take kinetics and mechanism and electroanalytical chemistry (elective) in the first semester, and transport processes (elective) and advanced organic (elective) in the second. Provision is made for individual study and thesis work for those who are interested and qualified. A one-hour course in chemical literature is also required.

A Course in Chemical Equilibria

The equilibrium course deals so intensively with quantitative relationships involving concentration that a good deal of attention and practice is given right at the start to problems involving molarity and volume. There is nothing novel here, although I might say polemically that I grant the concepts of normality and equivalence no consideration whatsoever.

Water as a Solvent

Since the course is primarily concerned with aqueous equilibria, it is logical to spend some time on the solvent itself. We discuss the properties and structure of water, the nature and consequences of hydrogen bonding, ionization, and the purification of water for chemical purposes.

Once the physical picture of pure water is reasonably clear, we begin contaminating it. After a brief review of the nature of the chemical bond, we consider the extent of dissociation of solutes, with emphasis on the inadequacy of only the two classifications of strong and weak.

Hydration is discussed for neutral molecules as well as for ions and, consistent with the spirit of the course, reference is made to recent literature. One of the pleasures of the course is the exposure of the *deficiencies* in our understanding and the need for additional research. For example, we look at values of ionic hydration numbers which are recent and respected, but the disagreement with other published values is not concealed.

The Activity Concept

It is pointed out that there will be interactions between the solute particles themselves. Electrostatic forces between ions are emphasized, but neutral molecule interactions are considered also. It becomes clear that such forces interfere with the free movement of solute particles, and the concepts of ideal and non-ideal behavior are easily introduced. The activity concept thus appears at this very early stage in the course. To be sure, the student as yet has little to which he can apply the concept, but this does not hamper his ability to realize that a factor such as the activity coefficient is a reasonable idea.

In accordance with the premise that a good subject should be treated deeply in the first exposure, we spend time on theories of activity coefficients.

The Setchenow equation for the activity coefficients of non-electrolytes in electrolyte solutions is illustrated by literature data such as the solubility of benzene in salt solutions (*4*).

The extended form of the Debye-Hückel equation (*5*) is presented with little apology for the lack of a derivation. After all, relatively few chemists understand the derivation even though they make regular use of the equation. We have here a relationship and concept too valuable to postpone until the senior year. Problems are assigned which involve both the theoretical calculation and the experimental determination of activity coefficients for both non-electrolytes and ions.

The study of this material is further reinforced in the laboratory, where the students determine the mean activity coefficient of silver bromate as a function of ionic strength. The experiment is not difficult. Each student prepares solid silver bromate simply by mixing solutions of silver nitrate and potassium bromate. The crystalline product is equilibrated with pure water and with a solution of potassium nitrate. The saturated solutions are analyzed for dissolved silver bromate by iodometric titration, using thiosulfate. The activity coefficient of silver bromate is calculated by comparing the solubility in the presence of potassium nitrate with that in pure water.

The students are thus introduced to analytical chemistry as an integral part of research. With each student working at a different assigned ionic strength, the many values of the activity coefficient are posted on a single large graph in the laboratory. The activity coefficient is plotted versus ionic strength, and each student places a map-tack according to his experimental value. The curve established by the tacks is readily compared with the prediction by the Debye-Hückel equation, and it is possible to deduce the constant in the Hückel extension term for this particular system. Through this experiment the effect of ionic strength and the concept of activity coefficient take on real meaning, especially because the student is using his own experimental data.

Reaction Rates and Mechanism

The chief reason for the section on chemical kinetics is the usual one, namely, its later use in the derivation of the equilibrium law. In contrast to common textbook practice, no attempt is made to write rate laws simply by using the coefficients in the over-all balanced equation (*6*), and a few examples are shown to illustrate the great variety of forms assumed by rate laws. The relationship between mechanism and rate law is emphasized. An excellent laboratory project for this part of the course is a quantitative study of the slow reaction between hydrogen peroxide and iodide ion at constant acidity (*7*). Through the interpretation of a few interesting clock reactions, the students calculate the value of the specific rate constant as well as the exponents to which the peroxide and iodide molarities must be raised in the rate law. Of course, considerable time is spent on the inorganic chemistry involved in the experiment.

The law of chemical equilibrium (which we do not

call the "law of mass action") is derived through kinetic reasoning for uni- and bimolecular reactions. The treatment is extended to more complicated reactions by considering them to have mechanisms which are series of uni- and bimolecular steps. For each individual step rate laws and equilibrium constants may be written, and it is shown that the over-all equilibrium constant is simply the product of all the stepwise constants. The data of Taylor and Crist (*8*) on the thermal decomposition of hydrogen iodide make excellent source material for discussion and problems on basic equilibrium principles. Finally, since the concept of activity has been made intelligible earlier, the relationship between the thermodynamic, or activity form, and the classical, or molarity form of the equilibrium constant is made clear.

Brønsted Acid-Base Concepts

In the section on acid-base equilibria, the Brønsted definitions are used exclusively, although part of the first lecture deals with their historical development. Pure water is considered *first*, not later as in many books, as the simplest example of an acid-base system. When solutions of acids and bases are discussed, the contribution by the dissociation of water is included, resulting in more accurate expressions for *p*H calculations. The primary virtues of the Brønsted concept are the simple conjugate relationship, and the realization that the electrical charge on a species is irrelevant to its classification as an acid or base. Mysteriously, many textbook writers do not seem to appreciate the elegance of this view and the great simplification which it permits. The so-called "hydrolysis" reaction is mentioned only as a nineteenth century complication which was forced by inadequate definitions, and the "ammonium hydroxide molecule" is exposed as a hydrogen-bonded structure (*9*).

This is the first section in the course which involves a large number of equilibrium problems, and to make such problems realistic the effects of ionic strength are considered intensively. Calculations are made as usual with classical constants involving molarity, but the values of the "constants" are corrected for the effect of ionic strength. It is shown that the classical value of any constant is easily related to the thermodynamic value by a collection of activity coefficients, which in turn are related to the ionic strength by the Debye-Hückel equation. A recent book by King (*10*) uses essentially the same approach. Reactions are classified by "charge types" to help generalize the effects of ionic strength.

In the laboratory work for acid-base many fundamental principles can be illustrated by a photometric determination of the dissociation constant of a weak acid such as dinitrophenol. It is possible to have the students do this visually, but only with crude results. It has seemed best to use a filter photometer and to do the experiment as a demonstration, letting the students take the data as a laboratory assignment. For this experiment, the principles of color measurement are treated in a simple empirical way. The color intensities of a series of acetic acid buffers containing known amounts of dinitrophenol are compared with a standard curve. By the time the data are carried through the many calculations required, most types of acid-base equilibria have been considered.

Complex Formation

Under the heading of complex formation we discuss the more common ligands and a few typical examples of complexes. In spite of the current recognition of the stepwise formation of complexes in solution, most textbooks still insist on showing the formation and dissociation of complexes in one over-all step only. This is followed by fallacious calculations which may be in error by factors in the millions. Such a practice is certainly a sad example of our failure to provide realistic information to our students.

The subject of complex formation prompts a consideration of inorganic nomenclature.

Solubility Equilibria

It is with the section on solubility equilibria that the new course shows the greatest deviation from the usual practice. Solubility equilibria are rarely as simple as the texts would have the student believe.

First, there may be appreciable amounts of undissociated material, even in solutions of the so-called strong electrolytes (*11*). It has been pointed out with authority (*12*) that complete dissociation appears to be the exception rather than the rule, and that for most aqueous electrolytes we are returning to the Arrhenius picture with the superposition of Debye-Hückel forces. Second, in addition to the fundamental solubility equilibria there are usually effects due to acidity and complex formation. The countless textbook problems which treat inorganic salts as if they were 100% dissociated with no complications are better described as oversimplified algebraic exercises than as fundamental chemistry. There are relatively few solubility systems which involve only a solubility product, and the usual generalization is seriously misleading to the student.

Since it is so difficult to generalize the subject of solubility equilibria, we take up a number of specific cases in detail to illustrate the varied nature of solubility systems. The first of these cases is the solubility of silver chloride in sodium chloride solutions.

The text of this material as it is covered in the course constitutes the accompanying paper.[1] We consider data on the solubility at low and at high chloride ion molarities (*13*) to determine the nature of dissolved silver chloride and the pertinent equilibrium constants. We begin by considering the data as a mystery, and proceed to analyze the results quantitatively by a series of plausible hypotheses and graphical interpretations. The discussion includes the experimental approaches used by the original researchers, and the goal of the material is to give the students a deeper understanding of the ways in which quantitative equilibrium studies can be used to clarify the inorganic chemistry of a system. It might be said that this material is simply a reliable journal article, rewritten, expanded, and reinterpreted for the sophomore. The student reaction to this material has been so gratifying that I am pleased to offer it as an example of what might well be done with many other cases in the literature.

The silver chloride study is followed by a rather similar treatment of silver acetate. The purpose of this section is to afford a basis for laboratory work, because silver acetate is soluble enough for ordinary

[1] See THIS JOURNAL, **37**, 348 (1960).

titrimetric methods to be used with accuracy. The students equilibrate solid silver acetate with a series of sodium acetate buffers of varying concentration. The saturated solutions are analyzed for dissolved silver by the Volhard titration, which has been covered thoroughly in the previous laboratory period. A plot of the observed solubility versus the reciprocal of the known acetate molarities is a straight line which may be used to determine the constant concentration of undissociated silver acetate and also its dissociation constant at the particular ionic strength. The linearity also establishes that higher acetato- complexes are not significant in the solutions. Thus, the students can again see the methods of analysis as a vital part of research, and the use of their own data teaches something about graphical methods which is not covered in the mathematics courses.

Continuing our discussion of selected solubility systems, we consider the solubility of copper iodate which depends upon acidity because of the formation of undissociated iodic acid. The solubility data are plotted to determine the solubility product for copper iodate and the dissociation constant for iodic acid. A student experiment on this subject has been described (*2*).

We also take up the study of solubility of diethylrhodanine, an organic analytical reagent for several metals. Sandell and Neumeyer (*14*) determined the solubility as a function of *p*H and showed that the two dissociation constants of the compound can be calculated.

Another worthy case for consideration is the solubility of ferrous hydroxide and the dissociation of the aquo ferrous ion, as studied by Leussing and Kolthoff (*15*). Needless to say, there are many other good possibilities for discussion in the recent literature, and the foregoing cases are mentioned as examples rather than as strong recommendations. I shall doubtless change my own examples from year to year.

In all of the solubility studies we pay careful attention to the experimental problems and approach as well as to basic principles. For example, in the discussion of ferrous hydroxide it is very worthwhile to point out the extreme difficulties associated with the need for working under strictly oxygen-free conditions. Such discussion is valuable for the "feeling" which it gives for the research. It should be emphasized that we try to make the solubility data work *for* us, to help answer some of the basic questions concerning the nature of dissolved substances, rather than to begin with all of the answers at hand.

Solvent Extraction

The next section of the course is subject to the same philosophy. The topic of solvent extraction equilibria has been unduly neglected in our curricula. First we discuss the close relation between solubility and extraction. This is followed by illustrations of the simple distribution law. For example, the distribution ratio of iodine between carbon tetrachloride and water is shown to be independent of concentration (*16*). However, like solubility equilibria, extraction equilibria cannot easily be generalized because of the large variety of effects which vary from system to system. Therefore we take up a series of examples illustrating in a gradual fashion the complications which are manifest in extraction systems. The first of the complications is illustrated by the extraction of acetic acid by ether, where the extraction ratio is not constant but varies linearly with concentration in the water phase (*17*). Dimerization is mentioned as a plausible hypothesis, and so we play around with algebra to see what would be the quantitative effect of such dimerization. If this interpretation fits the observed facts, we calculate the dimerization constant (*18*).

Other complications which we discuss include the effect of potassium iodide concentration on the distribution of iodine. This is used to demonstrate the existence of the triiodide ion and to determine its dissociation constant. The effect of *p*H on the distribution of an organic analytical reagent such as 8-hydroxyquinoline is studied to determine the acid-base characteristics of the reagent (*19*). The benzene extraction of antimony iodide (*20*) serves to illustrate complex formation and to show the need for further research. A logical conclusion to the series is the complicated system involving a metal chelate in the presence of excess organic reagent (*21*).

In all of these cases the technique is to look at some raw data, propose some ideas for explanation, derive some algebraic relationships, and then to assign the testing of the hypotheses as problem assignments to be completed outside of class. It is not a bad idea to include one or two cases where the proposed hypothesis is disproved rather than substantiated by the work of the students.

The section on solvent extraction ends with a discussion of volume-millimole relationships, including the application of extractive processes to the separation and concentration of materials.

The final section of the course is a brief consideration of analytical separations and qualitative testing, inorganic syntheses, etc. Such topics are examined in the light of the various types of equilibria which we have studied. The qualitative analysis scheme is described very briefly and provides some interesting separations and reactions for discussion.

Conclusion

I gladly admit that a great deal of further development is necessary. I trust that the course will evolve rapidly during the next few years. However, I am so strongly convinced that this approach represents a fundamental improvement in the teaching of electrolytic equilibria that I am willing to risk this somewhat premature presentation, with the hope that it will provoke further ideas and correspondence with interested persons.

Acknowledgment

The author is grateful to the National Science Foundation for a Science Faculty Fellowship during the summer of 1958, at which time the basic plan for the equilibrium course was developed and the writing on silver chloride was carried out.

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Solubility and Equilibria of Silver Chloride

Silver chloride competes with acetic acid for the dubious distinction of having the greatest number of equilibrium problems in chemistry textbooks. This position is not without some justification, for indeed silver chloride is of tremendous fundamental importance. It has long been used in qualitative analysis for the detection of silver and chloride, and it is even more valuable in the quantitative determination of these elements, the outstanding example being its intimate involvement in the establishment of the chemical values of atomic weights. Silver chloride has been of interest in photographic research because of its tendency toward decomposition when exposed to light, while in other optical work it is useful because of its ability to transmit light of long wavelength. As a component of the silver-silver chloride electrode it is of major importance in electrochemistry. The foregoing is not a comprehensive survey of its significance; so it is not surprising that technical articles concerning silver chloride are still appearing in the chemical literature at the rate of sixty or seventy per year. It is reasonable, therefore, to devote some time to a consideration of the nature of this classical compound in aqueous solution, with an indication of how such information is gained from experimental measurements.

It is not the purpose of what follows to give a comprehensive review of the research which has been carried out on silver chloride equilibria. Rather, a single contribution to the literature will be examined in some detail with an effort to show, through discussion and problems, some of the aspects of quantitative thinking.

We shall be concerned chiefly with a paper by J. H. Jonte and D. S. Martin, entitled "The Solubility of Silver Chloride and the Formation of Complexes in Chloride Solution."[1] The authors explain that one purpose of the work was to test the relatively new method of radioactive assay for the measurement of very small concentrations of substances in aqueous solutions. Another purpose was to obtain data concerning a region of chloride concentration not previously studied, thus extending our knowledge of silver chloride in chloride solutions.

The fundamental idea of the research is simply stated: to determine the solubility of silver chloride in sodium chloride solutions of varying concentration, and to interpret the results in terms of the various chemical equilibria operative in such solutions. In principle, "all" one has to do is to let solid silver chloride stand in contact with each of a series of carefully prepared sodium chloride solutions until no more will dissolve, remove a sample of the saturated solution, accurately analyze it for the silver content, and explain the findings. However, in practice not one of these four basic steps is a simple, routine matter. In the first place, one must use very pure chemicals and carefully prepared solutions, and special attention must be paid to the problem of actually attaining equilibrium. The temperature must

Editor's Note: Readers should note that this paper supplements that by the author which appears in this Journal, **37,** 344 (1960). It illustrates his philosophy of instruction in analytical chemistry there set forth.

[1] Jonte, J. H., and Martin, D. S., *J. Am. Chem. Soc.*, **74,** 2052 (1952).

be precisely controlled, and the time necessary for the solution to become saturated must be determined by repeated analyses. Second, the problem of removing a sample is critical, for one has to be careful that even very small amounts of solid silver chloride are not mistakenly included with the saturated solution. Also, during the sampling process it is essential that the temperature should not vary appreciably. Third, there are limits to the sensitivity of analytical methods, especially when precise results are necessary. Fourth, the theoretical interpretation of the experimental data is also subject to difficulty, as will be seen later.

Preliminary Speculation

Good research is not carried out blindly. The experiments must be planned carefully if they are to yield significant results, and a good deal of thinking and desk work must precede laboratory work. Such preliminary planning is always time-saving in the long run.

If we apply the general principles of solubility equilibria to the specific case of silver chloride in sodium chloride solutions, we postulate that the first step is the transfer of silver chloride molecules (ion pairs, if you prefer) from the solid state to the dissolved state:

$$\mathrm{AgCl\ (solid)} \rightleftharpoons \mathrm{AgCl\ (solution)}$$

The equilibrium constant for this "reaction" can be written as:

$$K_0 = [\mathrm{AgCl}]_s f_0 \qquad (1)$$

where the brackets indicate molarity, the subscript s indicates that the concentration is the maximum, the saturated value, and f_0 is the activity coefficient of the species which has a zero charge, the undissociated silver chloride molecule in solution.

Depending on the strength of silver chloride as an electrolyte, the substance is more or less dissociated into its ions:

$$\mathrm{AgCl\ (solution)} \rightleftharpoons \mathrm{Ag^+ + Cl^-}$$

and the equilibrium expression for this step is called the dissociation constant of silver chloride:

$$K_d = \frac{[\mathrm{Ag^+}][\mathrm{Cl^-}]}{[\mathrm{AgCl}]} \cdot \frac{f_1^2}{f_0} \qquad (2)$$

where f_1 is the activity coefficient of a singly-charged ion, making the approximation that the silver chloride ions have the same values. Notice that the subscript s is not written by [AgCl] in this case, because this equilibrium does not depend upon having a saturated solution.

If the solution contains excess chloride due to the presence of, say, sodium chloride, there is a tendency toward complex formation

$$\mathrm{AgCl\ (solution) + Cl^- \rightleftharpoons AgCl_2^-}$$

and we may write the formation constant of the complex ion as follows:

$$K_f = \frac{[\mathrm{AgCl_2^-}]}{[\mathrm{AgCl}][\mathrm{Cl^-}]} \cdot \frac{f_1}{f_0 f_1} \qquad (3)$$

where it is approximated that the activity coefficients of the singly-charged anions are nearly equal and therefore cancel.

There may also be the possibility of formation of higher complexes, such as $AgCl_3^{-2}$ and $AgCl_4^{-3}$, especially as the chloride concentration of the solution is increased to high values. The entire equilibrium system may be conveniently summarized in a scheme as shown in Figure 1.

Although it is conceivable that the system is even more complicated due to the formation of other ion pairs, we shall not include these possibilities in the discussion. Further, the fact that the hydrated silver ion (the symbol Ag^+ is merely shorthand for what is probably $Ag(H_2O)_2^+$) has a slight tendency to act as an acid,

$$\mathrm{Ag(H_2O)_2^+ + H_2O \rightleftharpoons AgOH(H_2O) + H_3O^+}$$

will also be ignored since it is such a weak acid that this reaction is virtually completely repressed by the small amounts of perchloric acid which were present in the solutions used by Jonte and Martin.

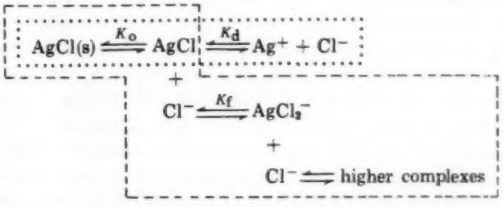

Figure 1. Equilibrium scheme for silver chloride in aqueous sodium chloride solutions. See text for significance of the dotted and dashed lines.

Figure 1 shows that the concentration of chloride ion should be instrumental in controlling the extent of the various equilibrium reactions, and hence the solubility of silver chloride. The next step is a consideration of the quantitative aspects of this control. A thorough discussion of this will be presented later under the heading of "Results and Discussion," but it should be realized that many of the quantitative ideas expressed in that section would have been considered by the experienced chemist *in advance* of the actual experimental work. Only in this way would he be able to plan the experiments well. And it is only a *very* well-planned experiment which will escape the need for repetition to correct the errors to which inexperience is vulnerable.

For the details of experimental procedure the reader is referred to the original article. Briefly stated, the radioactive assay method consists of evaporating the small sample of saturated solution to a thin film on a small copper disc. When this is placed near the Geiger tube, the amount of radioactive silver present can be estimated by comparison with the radioactivity observed when known amounts of silver are tested in the same way. The sensitivity depends on how "hot" the sample is.

Results and Discussion

It is sufficient for our purposes to limit our consideration to the data obtained at 25° C, as summarized in Table 1 and Figure 2. Notice that the chloride ion molarity varies tremendously, over a 2000-fold range. Then look at the very low values of molar solubility, which demand a very sensitive analytical method such as radioactive assay. Finally, and most significant, notice that the solubility at first decreases with increasing chloride concentration, passes through a *mini-*

Table 1. Data from Solubility Experiments with Silver Chloride at 25° C

Molarity of Cl^-	Solubility of AgCl (mol/liter)	Molarity of Cl^-	Solubility of AgCl (mol/liter)
5.38×10^{-5}	5.37×10^{-6}	1.27×10^{-3}	6.02×10^{-7}
5.92	3.31	1.59	5.62
1.12×10^{-4}	2.04	2.75	4.90
2.08	1.66	5.50	5.75
3.44	1.02	1.10×10^{-2}	6.60
5.51	6.92×10^{-7}	2.75	1.10×10^{-6}
9.66	6.92	5.50	1.95
1.10×10^{-3}	5.25	1.10×10^{-1}	3.80

mum at about 1×10^{-3} *M* Cl^-, and then increases steadily as the chloride concentration becomes greater.

At low concentrations of chloride ion, below about 10^{-3} *M*, apparently not enough is present to cause the formation of appreciable amounts of $AgCl_2^-$, let alone the higher complexes; so the equilibrium system is fairly well represented by the part of the equilibrium scheme (Fig. 1) shown within the dotted line. Restricting our consideration to this part, we can see why increasing chloride concentration at these low molarities causes a decreasing solubility. Chloride ion appears on the right side of the dissociation equation, along with silver ion. The more chloride ion in solution the more chances for collision with whatever silver ion is present, and hence the more formation of solid silver chloride, i.e., the lower the total amount of silver remaining in solution.

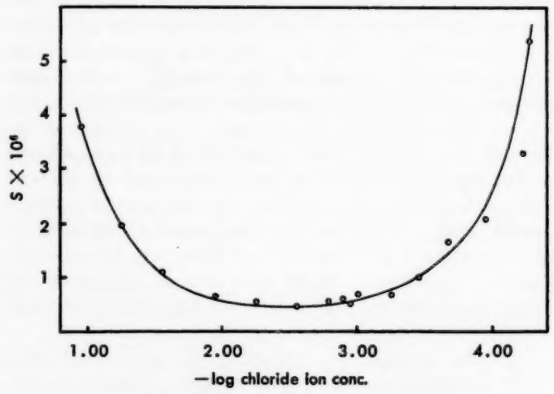

Figure 2. Solubility of AgCl in NaCl solutions (Jonte and Martin).[1]

On the other hand, as the chloride concentration becomes greater than about $10^{-3}M$, most of the simple silver ion is "driven" out of solution by the so-called common ion effect, making the dissociation reaction of little significance compared to the formation of complex ions. The system is then fairly represented by the part of Figure 1 enclosed by the dashed line. It is seen that the two parts are working in different directions. The common ion effect tends to reduce the solubility of silver chloride while complex formation tends to increase it. This accounts qualitatively for the minimum in the solubility as a function of chloride concentration. The minimum would occur approximately at the point where the effect of complex formation has increased sufficiently to just balance the common ion effect.

Perhaps the above conjectures sound reasonable, but how confident should one feel with just a qualitative explanation to back up his ideas? What is the relative significance of each of the various complex ions? Is the neutral form, AgCl, present in solution to an appreciable extent? Is the picture summarized in Figure 1 really sufficient to describe the actual system? Here we see the basic need for quantitative interpretation of experimental data. This is not to say that such interpretation will necessarily be free from fallacious thinking, but if the data follow the quantitative path predicted by the qualitative picture, certainly our belief in the truth of the picture will be greatly strengthened.

General Quantitative Relationships

Table 1 shows that there are two experimental variables: (1) the molarity of chloride ion, which is a *controlled* variable since it may be adjusted to any desired value by the addition of the proper amount of sodium chloride, and (2) the solubility of silver chloride, which may be called a *determined* variable. In order to test our explanation in a quantitative way we should derive a theoretical equation relating these variables and should determine whether the data are in quantitative agreement with the equation.

Assuming that our present picture of the equilibrium system is accurate, it follows that the solubility, *S*, is given by the following summation of the concentrations of silver-containing species:

$$S = [Ag^+] + [AgCl]_s + [AgCl_2^-] + [AgCl_3^{=}] + \ldots \quad (4)$$

Before going any further, let us make the tentative conjecture that in the solutions used by Jonte and Martin the chloride ion does not reach values high enough to cause the formation of appreciable amounts of the higher complexes. This will avoid the use of unduly complicated algebraic expressions. Of course, wishful thinking will be of no avail. That is, if the higher complexes are actually present in significant amount, we shall be forced eventually to consider them after all. But, for now, let us consider that the solubility is given fairly accurately by:

$$S \approx [Ag^+] + [AgCl]_s + [AgCl_2^-] \quad (5)$$

Equation (5) is not very useful to us in its present form. However, each of the three unknown terms on the right can be converted to an expression containing known quantities by application of the law of chemical equilibrium. From equations (1), (2), and (3) by rearrangement we find:

$$[AgCl]_s = K_0/f_0 \quad (6)$$

$$[Ag^+] = K_d K_0/[Cl^-]f_1^2 \quad (7)$$

$$[AgCl_2^-] = K_f K_0 [Cl^-] \quad (8)$$

When these expressions are substituted for the concentrations in equation (5), the result is

$$S \approx \frac{K_d K_0}{[Cl^-]f_1^2} + \frac{K_0}{f_0} + K_f K_0 [Cl^-] \quad (9)$$

This equation is the sort of thing we want, since it relates the solubility, *S*, to the chloride concentration of the solution. In addition to these two "major" variables, there are three constants, K_d, K_0 and K_f, as well as two other variables in the form of the activity

coefficients f_0 and f_1. Now, we have (Table 1) experimental values of S and $[Cl^-]$. The values of the constants are unknown, but at least they are constant, and it is one of our goals to determine their values if possible; and the values of the activity coefficients, while not known with high accuracy, are not completely out of reach. In the first place, f_0, the activity coefficient of the uncharged molecule, may be considered to be nearly constant and close to unity at the low ionic strengths employed. Further, we may not be too greatly in error if we assume that the values of f_1 may be calculated with reasonable accuracy from the theoretical equation derived by Debye and Hückel:

$$\log f_1 \approx \frac{0.51\,\mu^{1/2}}{1 + \mu^{1/2}} \qquad (10)$$

where μ is the ionic strength of a given solution, values of which were given by Jonte and Martin for each of their equilibrium solutions. Therefore it is merely a matter of calculation to obtain approximate values for the activity coefficients.

However, granted that equation (9) does not contain unknown terms other than the three equilibrium constants, how do we go about using the equation to test our earlier ideas and to determine the values of the equilibrium constants? There are various mathematical approaches to such a task, but the one most satisfying to many chemists is to examine the data graphically, according to a plan for which the equation predicts a straight line. Straight lines are pleasingly superior because the deviation of the experimental points from linearity is easily seen, and because the slopes and intercepts of straight lines are frequently of significance. Further discussion of our specific problem will clarify these generalizations.

Let us now apply to equation (9) the same kind of simplification used in our qualitative reasoning. That is, we shall again divide the experimental data into two parts—one at low chloride concentrations where complex formation is presumed to be negligible, and the other part at higher chloride concentrations where dissociation of AgCl into its ions is not significant.

At Low Chloride Concentrations

The third term on the right of equation (9) will be dropped since it represents the concentration of the complex ion, $AgCl_2^-$. Consequently we may write:

$$S \approx \frac{K_d K_0}{[Cl^-]\,f_1^2} + K_0 \qquad (11)$$

where f_0 has been omitted because of the approximation that it only has values close to unity. It should be emphasized that equation (11) is not intended to be valid except for conditions of low chloride concentration.

At first this equation might not look like one for a straight line, but we must beware of channeled thinking. The reader is doubtless familiar with the classical mathematics textbook equation of a straight line, $Y = mX + b$, where Y and X are variables, m is the slope of the line, and b is the intercept on the Y axis (the value of Y when X is zero). It is not difficult to see that equation (11) is of the same form, provided that one chooses the proper variables. The analogy is as follows:

$$Y = m \cdot X + b$$

$$S \approx K_d K_0 \cdot \frac{1}{[Cl^-]\,f_1^2} + K_0$$

variable = slope · variable + intercept

Therefore, if this equation is a satisfactory theoretical representation of the facts (i.e., of the data of Table 1), a plot of S versus the quantity $1/[Cl^-]f_1^2$ should be a straight line with a slope equal to $K_d K_0$ and an intercept

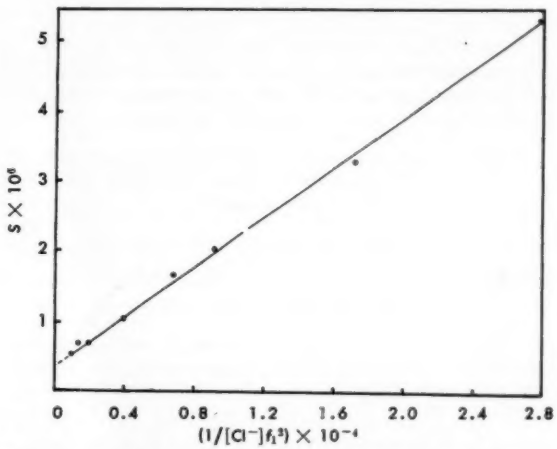

Figure 3. Interpretation of solubility data at low chloride molarities.

(on the S axis) of K_0. If such a plot does *not* turn out to be linear, the equation is not realistic, and we shall have to go back and reconsider our original hypotheses.

Table 2 shows the calculated values of the quantities necessary for making the graph. The values of $\mu^{1/2}$ were taken directly from the article by Jonte and Martin while the activity coefficients were calculated by using these values of $\mu^{1/2}$ in equation (10).

Figure 3 shows the appropriate plot. The experimental points lie close to the line, which was subjectively chosen as the "best" straight line through the points.

Table 2. Solubility Data for Silver Chloride at Low Chloride Molarities

S	$\mu^{1/2}$	f_1^2	$1/[Cl^-]$	$1/[Cl^-]f_1^2$
5.37×10^{-6}	0.206	0.670	1.86×10^4	2.78×10^4
3.31	0.008	0.982	1.69	1.72
2.04	0.011	0.974	8.93×10^3	9.17×10^3
1.66	0.167	0.715	4.81	6.72
1.02	0.138	0.752	2.90	3.86
6.92×10^{-7}	0.024	0.945	1.81	1.92
6.92	0.136	0.754	1.04	1.37
5.25	0.033	0.926	9.09×10^2	9.82×10^2
6.02	0.127	0.766	7.87	1.03×10^3
5.62	0.111	0.789	6.29	7.98×10^2

The slight scattering of points may be attributed to the experimental difficulties discussed earlier. The dotted portion of the line shows how it may be extrapolated to obtain the value of the intercept on the S axis, which can be read (on regular graph paper) as 3.5×10^{-7}. This, then, is the value of K_0 which we remember is the molarity of undissociated silver chloride molecules.

Equation (11) told us that the slope of this plot would be the value of the quantity $K_d K_0$. When we speak of "slope" in this connection, we do not mean slope in terms of degrees. Rather, we want the number which

expresses the rate at which the variable S changes with the variable $1/[Cl^-]f_1^2$. For example, we find from the graph that the value of S (according to the straight line) varies from 3.5×10^{-7} to 3.93×10^{-6} moles/liter when the value of the quantity $1/[Cl^-]f_1^2$ varies from zero to 2.0×10^4 liters/mole (activity coefficients are unitless). The slope is therefore calculated to be:

$$\text{slope} = K_dK_0 = \frac{(3.93 \times 10^{-6} - 0.35 \times 10^{-6}) \text{ moles/liter}}{(2.00 \times 10^{-4} - 0) \text{ liters/mole}}$$
$$= 1.79 \times 10^{-10} \text{ moles}^2/\text{liter}^2$$

Now we have obtained from this graph a value of K_0, the intercept, and a value of K_dK_0, the slope. We would not want to ignore the opportunity to combine these values to obtain a value for K_d alone:

$$\frac{K_dK_0}{K_0} = K_d = \frac{\text{slope}}{\text{intercept}} = \frac{1.79 \times 10^{-10} \text{ moles}^2/\text{liter}^2}{3.5 \times 10^{-7} \text{ moles/liter}}$$
$$= 5.1 \times 10^{-4} \text{ moles/liter}$$

When it is remembered that K_d is the dissociation constant for silver chloride, i.e., for the reaction,

$$AgCl \text{ (solution)} \leftrightharpoons Ag^+ + Cl^-$$

we reach the interesting and perhaps surprising conclusion that *silver chloride is a weak electrolyte in aqueous solution*. Of course, this conclusion (or the lack of this conclusion) depends upon one's definition of "electrolyte strength" (see problem 4 at the end of this chapter).

Let us now think about what we have done so far. From a general picture of the solubility of silver chloride in sodium chloride solutions (Fig. 1), we extracted a simplified view by imposing the condition of low chloride concentration. Restricting our attention to this view, we derived an equation which told us how the solubility *ought* to depend upon chloride concentration, if our view was correct. We then showed by a graphical method that the actual experimental data did indeed seem consistent with such a theory (equation 11) provided that the numerical values of the two equilibrium constants were $K_0 = 3.5 \times 10^{-7}$ and $K_d = 5.1 \times 10^{-4}$. In other words, we not only obtained strong evidence for the truth of the qualitative picture, but determined the quantitative relationships governing the picture as well.

Therefore, let us proceed triumphantly to a consideration of the rest of the data, namely, the region of chloride concentration where complexes are formed.

At Higher Chloride Concentrations

The dissociation of silver chloride into its ions will be repressed nearly completely. Now that we have the value of the dissociation constant, K_d, we can back this claim up with a simple calculation: Suppose we take one of the lower values of chloride concentration to be considered in this section, for example $0.01\ M$. In the saturated solution the concentration of undissociated AgCl will be constant and equal to 3.5×10^{-7}. We may then calculate the concentration of ionized silver by using an equation (7), leaving out activity coefficients for simplicity.

$$[Ag^+] \approx K_0K_d/[Cl^-] = 3.5 \times 10^{-7} \times 5.1 \times 10^{-4}/0.01$$
$$\approx 1.8 \times 10^{-8} \text{ moles/liter}$$

This concentration is small enough, compared to the total solubility (about 7×10^{-7} at that point), that the error in leaving it out of our consideration is small, and the error becomes far less important as the chloride concentration becomes still greater.

Therefore, the first term on the right of equation (9) will be dropped, since it represents the concentration of the free silver ion, and the simplified equation may then be written as:

$$S \approx K_0 + K_fK_0[Cl^-] \quad (12)$$

This equation is of the form of a straight line provided that the variables plotted are S and $[Cl^-]$. The intercept would be K_0 and the slope would be the product K_fK_0. For the reason given earlier, the activity coefficient of the neutral molecule, f_0, has been omitted. Notice that there are no ionic activity coefficients because, as mentioned under equation (3), it is presumed that the activity coefficient for the $AgCl_2^-$ ion is nearly equal to that of the chloride ion.

Table 1 (right-hand columns) therefore contains the data necessary for the preparation of a graph according to equation (12), and Figure 4 shows the plot.

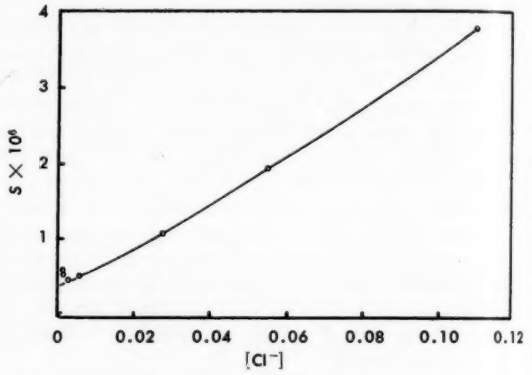

Figure 4. Interpretation of solubility data at higher chloride molarities.

Here we see a type of situation which is not uncommon in research. We have been working with a hypothesis which predicted that the plot would be a straight line, and when the points are actually plotted, they seem to fall on a curve, slight but smooth. This suggests that the solubility depends (at least in part) upon the concentration of chloride raised to a power higher than unity. This, in turn, implies that we were incorrect in completely ignoring the formation of the higher complexes at these chloride concentrations.

But now, before we get carried away, let us pretend that we have a friend, notorious for his skepticism, who looks at Figure 4 and says, "There's no need to consider that as a curve. It is probably a straight line, with small experimental errors such as those evident in Figure 3 causing a random scattering of points which just happen, by sheer coincidence, to fall on a smooth curve!" This would sound attractive if we "wanted" the line to be straight. Even if we adopted that attitude so rare to humans, the completely open and unprejudiced mind, we should have to admit that the argument of the friend could not be dismissed lightly. Of course, if we were actually prejudiced toward viewing the plot as a curve, we might try to discredit that argument by saying that "it would indeed be highly unlikely" that the data would accidentally fall on a curve as nice and smooth as this one!

Where does all this leave us? Don't scientists start

with precise measurements and proceed by strict logical steps to incontrovertible conclusions?"[2] What is wrong that we should start arguing over something which ought to be objectively clear? *Is it not the small number of experimental points which we are using to make up the plot of Figure 4?* If we had, say, a half dozen more experimental points distributed uniformly in the same region of chloride concentration and the results *still* indicated a smooth curve, the argument about chance scattering would have little strength. On the other hand, it might be that the additional points would indicate that a linear relationship did exist.

Of course, the difference between a straight line and a slight curve is not a "black or white" situation. The degree of curvature, or deviation from a straight line, is important in deciding whether it is significant or not. For example, in the present case we might feel that even if the experimental points are sufficiently precise to establish a curve, the deviation from linearity is not so great that we are prevented from estimating an approximate value of the quantity $K_f K_0$. (See problem 5.) Nevertheless, we still conclude that it is desirable to gather more data on this system in order to settle our problem more precisely.

The problems which follow are not merely exercises. They are designed to continue the discussion and to present some further ideas about silver chloride.

Problems

1. In this chapter, the silver chloride equilibrium system has been pictured in a way which makes natural the consideration of the equilibrium constants defined as K_0, K_d, and K_f. However, many chemists like to consider the following equilibrium constants:

$$K_{sp} = [Ag^+][Cl^-],$$

the solubility product,

$$K_i = \frac{[Ag^+][Cl^-]^2}{[AgCl_2^-]},$$

the instability constant of the complex ion, and

$$K = \frac{[AgCl_2^-]}{[Cl^-]},$$

the constant for the formation of the complex ion from solid silver chloride, i.e., for the reaction: AgCl (solid) + $Cl^- \leftrightharpoons AgCl_2^-$.

Show (ignoring activity coefficients) that each of these constants may be considered as a combination of the constants K_0, K_d, and K_f, thus demonstrating that these three are entirely sufficient to describe the system.

2. Perhaps the most common textbook problem concerning silver chloride is as follows: "Given that the solubility product of silver chloride is about 1×10^{-10}; calculate the solubility of silver chloride in 0.1 *M* potassium chloride." The inevitable textbook answer to this problem is that $S = 1 \times 10^{-9}$ moles/liter. Criticize both this answer and the statement of the problem thoughtfully and thoroughly, and rewrite the problem in a more meaningful and realistic way.

3. Using the values of the equilibrium constants derived in this chapter, calculate the solubility of silver chloride in pure water, assuming that complex formation is negligible and that no appreciable amount of AgOH is formed in the neutral solution. Ans.: 1.37×10^{-5} *M*.

4. Chemist A defines a strong electrolyte as one which is completely or almost completely dissociated into its ions in water solution (no other substances being present). Chemist B, however, feels that a better definition is based on consideration of the value of the dissociation constant, for example weak electrolytes being those with dissociation constants less than about 1×10^{-2}. How would silver chloride be classified by each of these chemists? How might this paradox be avoided?

5. Assume that you are prejudiced toward the "straight line" interpretation of the data of Figure 4. Draw the best straight line through the data and use the intercept and slope to calculate the supposed value of K_f. Ans.: 1×10^2.

6. In a later paper [*Sartryck ur Svensk Kemisk Tidskrift*, **65**, 88 (1953)], Berne and Leden suggested that the work of Jonte and Martin may have suffered from lack of complete centrifugation since their observed value of the molarity of undissociated silver chloride is about twice as high as that estimated by other workers. These authors say: ". . . and hence it is perhaps possible that small solid particles, mentioned above, were not entirely separated from their solutions, which should result in too high solubilities and thus in high values of their equilibrium constants, too." What might you offer in opposition to this suggestion? How confident do you feel about it?

7. It might be expected that formation of the higher complexes would become negligible compared to formation of $AgCl_2^-$ as the chloride concentration approached low values. Thus, assuming that the plot of Figure 4 is indeed a true curve, it would be expected that the slope of the curve would approach the value of $K_f K_0$ at the lower chloride molarities. Estimate the value of the limiting slope of the curve of Figure 4 by drawing a straight line which passes through 3.5×10^{-7} on the *S* axis and which is tangent to the smooth curve. Berne and Leden (see above) list the probable value of this quantity, $K_f K_0$, as $(2.0 \pm 0.2) \times 10^{-5}$.

8. In *Chemical Abstracts* [*C.A.*, **49**, 3622d (1955)], is found the following account (not an exact quote) of some work by Fomin: "The solubility of silver chloride was measured in aqueous solutions of NaCl at 25°C. The solubility can be represented by the equation, $S = 4.2 \times 10^{-5} \times C + 5.4 \times 10^{-7}$, where *C* is the molarity of NaCl." Since this is the equation of a straight line (compare with equation 12 in the text), it would seem from this abstract that Fomin has succeeded in settling a controversy in favor of the hypothetical skeptical friend referred to earlier. Draw a line on Figure 4 corresponding to this equation of Fomin's, and compare it with the data of Jonte and Martin. What would Berne and Leden think of this? Calculate the value of K_f using these new data. Ans.: 78.

9. After reading the abstract quoted in problem 8 it was desired to examine the original article by Fomin [*J. Phys. Chem.* (*U.S.S.R.*), **27**, 1280 (1953)]. A friend who knows Russian helped us deduce that Fomin's experimental results are:

Molarity of NaCl	Molar solubility of AgCl
3.86×10^{-3}	0.72×10^{-6}
9.24	0.91
1.76×10^{-2}	1.31
3.65	1.89
8.84	3.61
3.56×10^{-1}	1.74×10^{-5}
5.11	2.80
9.33	8.60

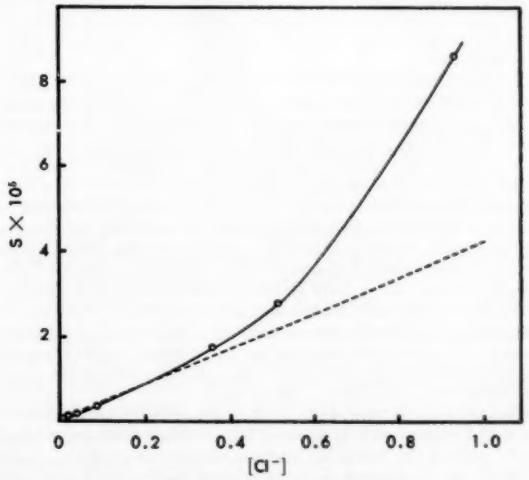

Figure 5. Solubility of AgCl in NaCl solutions (Fomin).

[2] See HILDEBRAND, J. H., "Science in the Making," Columbia University Press, **1957**, p. 7.

These data are summarized in Figure 5. The dotted line is that which is consistent with the equation given in the abstract.

(*a*) What do you think of the adequacy of the abstract?

(*b*) Does problem 7 suggest a way to improve the abstract?

(*c*) How do these results tie in with the controversy discussed earlier about the data of Jonte and Martin at higher chloride molarities?

10. The following results are reported by Barney, Argersinger, and Reynolds [*J. Am. Chem. Soc.*, **73**, 3785 (1951)], on the solubility of silver chloride in potassium chloride solutions:

Molarity of KCl	Molar solubility of AgCl
1.00×10^{-3}	1.60×10^{-7}
1.50	1.55
2.00	1.76
4.00	2.01
5.00	2.32
10.0	3.20

Compare these data with the other sets presented, with special attention to the problem of making an estimate of the concentration of undissociated silver chloride and the value of K_f. Assume that no complexes higher than $AgCl_2^-$ are formed.

The case of silver chloride has been presented in some detail, not only because of the importance of the compound itself, but especially because of the opportunity to show some of the approaches and thinking involved in equilibrium research. In general, the pattern consisted of forming a qualitative picture of the equilibrium system, deriving the quantitative relationships which would be expected to govern the hypothetical system, testing these relationships by graphical presentation of the experimental data, and finally paying attention to the deviations of the data from the expected path. In this particular case the deviations were not large, nor were they very difficult to explain, but it was clear that more data were needed to settle the questions. Often in research the deviations are not easily explained, and the chemist begins the challenging and highly satisfying process of what is loosely called "creative thinking." Sometimes an entirely different approach to the problem is necessary before the answer can be found. We have also seen that the results of different workers do not always agree. In principle they may all be studying the same thing, but in practice, due to experimental difficulties and varied approaches, they may actually be measuring somewhat different quantities. This points up the great need for careful planning of each experiment. Ideally, the researcher should know not only what he *wants* to measure, but also that he is truly measuring that quantity. It is difficult to choose the "best" results on silver chloride from the several sets of data in the literature, but it is obvious that they cannot all be right and perhaps none are free from criticism. Thus, there is still an opportunity for someone to carry out further measurements on silver chloride solubility, even if his work merely confirms the findings of one of the previous workers.

The Case of the Missing Joules—a Chem Gem Necklace

Inspector Sherlock Ohms, of Standard International Yard, was driving across the Wheatstone Bridge in his '09 Maxwell. He was trying to remember Ava Gadro's number so he could call and data for the Policeman's Ball—when suddenly he blew a tire. "OH^- Nernst" said Sherlock, "I dont have a tire ion with me, but luckily ammonia short distance from the Ideal Gas Station." (This business was handled by Saul Vent, who, at the moment, was freon bail.)

Just as the inspector emerged from the station, a rubber policeman whizzed by on his Carnot cycle. Ohms knew he was deuteride by, but he wondered watt made him rush so. He shouted atom, but he was gone. Ohms' reaction was instantaneous. By radio activity he learned that Micro Farad, Recipro City's top-ranking rookie, was chasing a joule thief.

Ohms chased Mirco down Elect Road, around the Elastic Modulus, back over Salt Bridge and up into Farren Heights. He turned left at the Old Ball Mill, went past the Mono Clinic, the Palladium, and all the way to the liquid junction at Endothermic Street. They were almost across the city line when Sherlock's car swerved and crashed into a Van der Waal. The impact splintered the Plancks and punched a big hole in the hydrolysis system. "I node that was going to happen," said Sherlock, "but I'd beta catch up to him." Quickly he volted out of his rect ilinear and took up the chase on foot.

He soon came across Micro, standing in a magnetic field, holding Ann Hydrate and Al Doll at bay. "Watts the meaning of this?" queried the Inspector, and the copper was quick to explain.

"Well, Sir, I stopped in at the Invar Bar, a local dyne and dance spot, for a couple of quartz of Lambert Beer when I noticed Ann Hydrate sitting alone at a two-place log table. I knew some joule thieves had made a radon Ethyl Benzene's country estate, and I spotted one of the Benzene rings on her, along with a para Ethyl's earrings.

"Anode an explanation of this, but before I could torque to her, she was in her coat of rust and out the door. Being true to the Kopp's Rule, I was quick to follow; but when she got into her Monochromatic-8, I knew I was infra tough chase. Fortunately her engine started Fehling just beyond the city limits and I caught her.

"She had led me to the missing joules, and also to her accomplice Al Doll who was about to barium in a hollow common log, under the square roots of this deserted magnetic field. While we were waiting for you, their other partner Cal Orie tried to run me down with his Mercury. Did that make my blood Boyle! I dodged and hit him with a bag of Boltz . . . man! Did that change his molar concentration!

"But really, Inspector, there wasn't any trig in catching these joule thieves. I just Van't Hoff on a normal lead—don't you zinc that explains it?"

Inspector Ohms beamed. Son, you'll go on nights for this!" (In effect, this was a promotion—for in Recipro City, nitrates are much mohr than those faraday man.)

EDITOR'S NOTE: This Gem was brought to our attention by Mr. Gene Doty, Hillsboro Union High School, Hillsboro, Oregon. So far, no one admits authorship. Readers having information about its source are invited to correspond with the Editor.

Karol J. Mysels
University of Southern California
Los Angeles 7

A Survey of Course Offerings in Colloid and Surface Chemistry, 1959[1]

More than ten years ago a symposium[2] reviewed the philosophy and content of courses and textbooks in colloid chemistry. There seems to be no readily available information, however, on the emphasis on colloid and surface chemistry in the standard general courses, on the availability of specialized courses, or on the attitudes of the academic world toward these fields. Yet any evaluation of the professional training in these important areas and any action to assure that this training is adequate requires factual information about these points. The present paper presents some pertinent data obtained by a survey among the ACS-approved departments.

The Survey

The survey covered the 262 departments on the ACS-approved list for 1958.[3] Four separate questionnaires went to each school addressed to the chariman, and to the professors of freshman chemistry, quantitative analysis, and physical chemistry. The chairmen were asked questions about the offering and description of any specialized course. Their opinion about the change which occurred in emphasis on these fields during the ten years and how it should change in the future was also solicited. The professors were asked about the amount of time spent on colloid and surface chemistry in their courses, the texts used, and the principal departures from the text. Comments were also invited. The questionnaires were mailed out in February, 1959, on divisional stationary[4] over the signature of Professor Ralph A. Beebe and the author.

The questionnaires were *not* anonymous. Each carried the name of the institution to which it was addressed, and many respondents signed their answers. This permitted a correlation of the answers with the size of the school. A convenient measure of this size was found in the number of graduating bachelors[5] certified by the school in 1958. A related quantity was the number of Ph.D.'s granted in the field of chemistry[5] in the same year.

Of the 1048 questionnaires sent out, 702 (67%) were returned. The rate of return was highest for the chairmen (78%), and lowest for professors of quantitative analysis (54%). Of the 262 schools, all four answers were received from 84 (31%), while only 14 schools (5%) representing about 2% of the students did not return any information.

While most replies were informative, some omitted important data. Frequently, if the professor gave a specialized course in colloid and surface chemistry in addition to one of the basic courses, his response dealt with the former instead of the latter. There is also obviously much difference of opinion about the scope and meaning of the term "colloid and surface chemistry." Some respondents explicitly excluded such topics as heterogeneous catalysis or macromolecules from these fields; others included them just as explicitly.

Results

Specialized Courses. Seventy-seven schools have a separate course in surface and/or colloid chemistry open to undergraduates. In six of these schools, the course is required for chemistry majors. On the other hand, some of these 77 courses are not given regularly, and in a few cases, have not been given for several years. Not included in this total are 7 schools which had such a course in the past but discontinued it, nor 10 schools which are considering adding one. One of the 77 schools has the course outside of the chemistry department, and at least 5 have such courses both within and without the department. A graduate course not open to undergraduates is offered in 12 other schools.

In the following, the 89 (77 + 12) schools in which there is an active teaching program in colloids and surfaces are grouped together as schools *with* (a colloid course). The others are denoted as *without*. In view of the relatively complete replies received, especially from schools *with*, it is likely that this division is quite accurate as far as the approved schools are concerned. It does not seem probable that there is a significant number of schools *with* among the non-approved ones.

These 89 schools *with* represent 34% of the approved schools and graduate 44.5% of the certified bachelors and 53% of the Ph.D's in chemistry. This suggests strongly that a separate course is much more likely to be encountered in a large school than in a small one. A closer analysis of the data showed that among schools graduating less than 15 B.S.'s per year, the *with* are a minority while they are a majority among the larger ones. The median school *with* graduates 9 bachelors while that *without*, only 4 of them; the median B.S. *with* is part of a class of 16 while the one *without* is in a class of 10.

There are some regional[6] differences, the school *with*

[1] Based on a committee report presented to the Division of Colloid Chemistry at the 136th Meeting of the American Chemical Society, Atlantic City, N. J., September, 1959. The committee, consisting of Professor Ralph A. Beebe, Amherst College, and the author, was appointed in the spring of 1958 to study the teaching of colloid chemistry. Copies of the complete report are available from the author.

[2] J. CHEM. EDUC., **26**, 18–31, 60 (1949).

[3] *Chem. Eng. News*, **36**, 14, 99 (Apr. 7, 1958).

[4] The division authorized the survey and contributed toward its cost at the fall, 1958, meeting.

[5] *Chem. Eng. News*, **37**, 13, 109 (March 30, 1959).

being less frequent in the northeast: 25.5% versus 39–40% in the other parts. This is due mainly to the larger size (10 B.S.'s/yr.) of the median school *with* in this region. Smaller schools are more likely to offer a separate course in the rest of the country, especially in the southeast (6.5 B.S.'s/yr.).

Inclusion in General Courses. The amount of time spent on colloids and surfaces in the standard undergraduate courses varies enormously from school to school. Part of this variation must be due to the semantics of the term, but much of it is probably real. About 10% of the teachers in each course reported that they spent no time at all on these subjects. The median time devoted is slightly over 1 hour in the freshman course, almost 2 hours in quantitative analysis, and almost 5 hours in physical chemistry. The distribution then rises gradually to a maximum of about 4, 6, and 12 hours respectively in the three courses.

One could speculate that in schools *with* there would be in general more emphasis on the subject throughout the curriculum or alternately that there would be a tendency to leave the subject to the specialized course. Comments indicate that both trends exist, but an analysis of the reports shows that they must neutralize each other as there is no significant difference between the schools *with* and *without*. This comparison may be somewhat biased by the fact that many of the professors teaching a specialized course did not provide data concerning their general course. Hence their courses are missing from the *with* category. This would cause the biggest error in the physical chemistry course where 14% of the *with* responses are thus removed, and only 40% of the *with* gave usable answers. The bias is about half as large in quantitative and negligible in freshman chemistry.

Attitudes of Chairmen. Almost one-third of the chairmen feel that the emphasis on these fields *has* decreased in the past ten years and only a negligible minority believe that it *should* be decreased in the future. In contrast, more than a third feel that the emphasis *has* increased and almost half believe that it *should* increase.

A cross-correlation shows that while the largest group of charimen (20%) is favorably disposed to past and future (*has* +, *should* +) there is a very small group (1%) in the (*has* −, *should* −) category and a very substantial one (10%) in the (*has* −, *should* +) combination.

[6] The boundaries used included Virginia, Tennessee, Kentucky, Mississippi, and Louisiana in the southeast; Wisconsin and Illinois in the central; and Montana, Wyoming, Colorado, and New Mexico in the west.

Again there was no significant difference in attitudes between chairmen of departments *with* and *without*. This was true only of chairmen who did express their opinion. There seemed to be a significant difference in the attitude of the chairmen toward the survey itself depending on whether they were in the *with* category or not. Ninety-six per cent of the former returned the questionnaire and 84% expressed an opinion about emphasis. In contrast, only 77.5% of the chairmen *without* answered and only 57% expressed their opinion.

Comments of Respondents. Several hundred comments ranging from a few words to a few pages were received but are difficult to summarize because of the great divergence of views expressed on a variety of aspects of the survey. One of the most frequent comments dealt with the low emphasis on the field. Limited time, subject too specialized or less fundamental than others, were the principal reasons given. The discontinuance of the course was often linked with the retirement of a faculty member and its initiation conditioned upon the finding of suitable personnel. This suggests that the subject is frequently unfamiliar to the average faculty member.

It may be worth noting that while there were more than 10 comments deploring the poor or inadequate preparation of the undergraduates in these fields, there was only one complaining about too much time and emphasis on colloids and surfaces.

Summary

The emphasis and time devoted to colloid and surface chemistry varies greatly from department to department. In basic courses, 1 hour is devoted on the average to this subject in freshman chemistry, 2 hours in quantitative analysis, and 5 hours in physical chemistry. The number of specialized courses offered is substantial, but they are much more likely to be encountered in a school having a large group of chemistry majors. Departmental administration is disposed on the whole favorably or at least neutrally toward the field. There seems to be no correlation between the offering of a specialized course and either the time devoted to the subject in the basic curriculum or the attitudes of the chairmen.

Acknowledgment

It is a pleasure to acknowledge the help of Professor R. A. Beebe in preparing the survey and this manuscript. Miss J. Hotchkiss was very helpful in the tabulation of the data.

Science Books for Secondary Schools—1960 Supplement

The Connecticut Science Teachers Association has proposed a supplement to its original Bibliography published in 1958. This pamphlet adds 165 titles to the 525 previously listed. Titles are annotated and are grouped under 15 subject categories. Copies are available for 35 cents from Professor R. Vincent Cash, Central Connecticut State College, New Britain, Connecticut

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Philadelphia 44, Pennsylvania

The Chemical Library of Thomas Jefferson

Thomas Jefferson, third President of the United States, is well known to have had a profound interest in the sciences, credit for which he ascribes, in no small part, to Dr. William Small, one of his early teachers. Jefferson mentions that it was his great good fortune that Small was a teacher of mathematics when he attended college and that they became friends. For, says Jefferson, "[F]rom his conversation I got my first view of the expansion of science and of the system of things in which we are placed."[1]

In Jefferson's love of the sciences there was plenty of room for chemistry, as we can see from the following quotations:

> . . . speaking one day with Monsieur de Buffon on the present order of chemical enquiry, he affected to consider chemistry but as cookery, and to place the toils of the laboratory on a footing with those of the kitchen. I think it on the contrary among the most useful of sciences, and big with future discoveries for the utility and safety of the human race. It is yet indeed a mere embryon . . .
> (Letter to the Reverend James Madison, July 19, 1788)
> . . . I have wished to see their [the chemists'] science applied to domestic objects, to malting, for instance, brewing, making cyder, to the making of bread, butter, cheese, soap, to the incubation of eggs etc."
> (Letter to Thomas Cooper, July 10, 1812)

The last quotation shows his very special interest in chemistry as applied to the household, to industry, and to human health. Writing to Dr. Thomas Cooper in July, 1812, he expresses a similar hope that Cooper will make the chemistry of such household articles "intelligible to our good house-wives." Earlier (August, 1805), he had written to Dr. Thomas Ewell of the importance of applying chemistry to the household arts. (His friend, Dr. Benjamin Rush,[2] was of similar opinion, having already given a course in chemistry of the home in the year 1787, at the Young Ladies' Academy of Philadelphia.)

Other indications of Jefferson's very high regard for the utility of chemistry come from the large number of English, French, and Italian chemical books in the "Technical Arts" section of his library. Some of these deal with brewing, fruit cookery, syrups, etc.

While on tour of western Germany, northern Italy, and southern France he "scouted" the wine-making, olive-oil-expressing, rice-milling, hay-curing, and butter- and cheese-making industries for the benefit of America, thus also giving further evidence of his deep interest in the applications of chemistry. He maintained this interest throughout his lifetime and wrote in 1818 (to Benjamin Waterhouse) that he was confident of "advances by the present generation and have no doubt they will consequently be as much wiser than we as we than our fathers were."

Further evidence of Jefferson's interest in chemistry was his attempt to give the subject very great prominence among the courses of study to be pursued at the university which he planned at Charlottesville.

There was so marked a resemblance between him and Joseph Priestley in intellectual tastes and the liberal views which both of them held on religion, philosophy, and politics that it was a most natural consequence that they should have been, and indeed, were, fast friends. It is a matter for conjecture as to how many of the ideas behind the project at Charlottesville originated in Priestley's "Hints Concerning Public Education," which the latter wrote in the year 1800 at the request of his friend Jefferson, whose interest and tendency to keep up to date in chemistry did not suffer from this association. (The espousal of the phlogiston theory by the learned doctor must have helped incline the statesman toward acceptance of the same theory.[3]) Jefferson's enthusiasm for chemistry carried him further than did Priestley's. Writing, on May 2, 1826, only two months before his death, to Dr. John P. Emmett, professor of natural history at the new university, Jefferson suggested that this year's course consist of *one* dozen lectures each of botany, zoology, mineralogy, and geology and *eight* dozen of chemistry. (He also advocated education in science as a groundwork for later training of those who planned careers in law or politics, as well as for assuring America the technologically-trained manpower needed for the development of our natural resources.)

Jefferson had a scientific mind by nature and upon graduation from college his mastery of the physical sciences was rare for his age. His "Report on the Methods of Obtaining Fresh Water from Salt" tells of the experiment which he carried out in March, 1791, with Rittenhouse, Wistar, and Hutchinson, while he was Secretary of State.

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[1] "Writings of Thomas Jefferson," PAUL FORD, editor, 1, 4.
[2] For more information on Rush, see THIS JOURNAL, 18, 555f (1941).

[3] While it is true that Jefferson owned works by the phlogistonists, Scheele, Priestley, Ingenhousz, Macquer, etc., he also found a place in his collection for the anti-phlogistonists, Lavoisier, Fourcroy, Berthollet, and Guyton de Morveau.

To Dr. James Currie of Richmond, Va., he wrote, ". . . You have heard of the new chemical nomenclature endeavoured to be introduced by Lavoisier, Fourcroy & [o]ther chemists of this country, of equal note, reject it, and prove in my opinion that it is premature, insufficient, false. [T]hese later are joined by the British Chemists, and upon the whole I think the new nomenclature will be rejected after doing more harm than good. [T]here are some good publications in it, which must be translated into ordinary chemical language before they will be useful . . ."

Minutes of the American Philosophical Society, Dec. 17, 1779: "Mr. Rittenhouse communicated to the Society, letters from the Rev.'d Mr. Maddison, President of William & Mary's College in Virginia containing a Series of meteorological observations by his Excellency Governor Jefferson and himself seperately for an year and an half; likewise a set of Experiments on what are called the sweet springs." (The experiments on the water of sweet springs were on qualitative analysis—chlorides, sulfates, acidity or alkalinity, etc. However, no evidence has been uncovered to enable us to associate Jefferson's name with the chemical portion of Madison's report.)

This report, the first chemical document ever published by the Government of the United States, has become a classic. Again, to du Pont de Nemours, he writes, "Nature intended me for the tranquil pursuits of science, by rendering them my supreme delight." His reading and personal correspondence kept him abreast of the latest developments, including those of chemistry. His "Notes on the State of Virginia" (1782) included a discussion of the mineral, animal, and vegetable resources of the state, and won a place of highest scientific esteem, laying the foundation for his fame as a "pioneer scientific man" of America.

Perhaps the evidence of Jefferson's interest in chemistry which can claim primacy, however, is his collection of books on the subject, because for him the importance of a subject and the degree of its utility were reflected in the number of books on it that he owned. He tells in a letter to Congressman Samuel H. Smith, of devoting every free afternoon for a summer or two, while residing in Paris, to visits to all the principal book stores, "turning over every book with my own hand and putting by everything . . . rare and valuable in every science . . . and after my return to America . . . the collection which I suppose is between nine and ten thousand volumes . . includes what is chiefly valuable in science and literature . . ."

When Jefferson's library was purchased by the United States government in 1815[4] and became the nucleus of the Library of Congress, it was the finest private book collection in our land and comprised more than six thousand volumes. (Of these only a third survives, due to the ravages of time and the fire of 1851, during which the chemistry section escaped destruction. But Jefferson's books have had a strong influence upon the growth of the Library of Congress and are revered among the chief treasures of the library.) Jefferson is known to have owned and sold to the government, in 1815, thirty books on chemistry, of which the Library owns twenty-eight from the original collections and two replacements for the two missing ones. For his time, that would have been a good collection and gives evidence of a concern for the subject more eloquent, perhaps, than words alone could be.

An interesting sidelight is the fact that Jefferson did not use a book-plate. Instead, whenever a printer used a "T signature" at the bottom of a page, Jefferson would complete his initials by inscribing the letter "J" after or by inscribing a "T" before the printer's "I" (for "J").[5] By this secret and ingenious method, he was able to hide his initials in every book. Other means of identifying Jefferson's books are by the author's presentation inscription on the flyleaf or by the "Georgetown" binding.

Below is a bibliography of Thomas Jefferson's chemistry books, in the order in which they appear in the Library of Congress Catalogue.

MACQUER, PIERRE JOSEPH, "Elements of the theory and practice of Chemistry." Translated from the French by Andrew Reid, 2 vols., London, 1758.

A few corrections, in ink, perhaps by Jefferson.

NEUMANN, CASPAR, "The Chemical Works of Caspar Neumann, M.D., Professor of Chemistry at Berlin . . . containing later Discoveries and Improvements," London, 1759.

This is one of the only two books which the Library has had to replace in the Jefferson Collection. Neumann (1683–1737) was a Fellow of the Royal Society.

CRAMER, JOHANN ANDREAS, "Elements of the Art of Assaying Metals." In Two Parts. The First, Theory; the Second, the Practice of the said Art . . . by John Andrew Cramer, M.D. Translated from the Latin by Cromwell Mortimer. With an Appendix containing a list of the chief authors that have been published in English upon Minerals and Metals. London, 1741.

Cramer (1710–77) was a German chemist and Counsellor for mines and metallurgy at Blankenburg. Mortimer was an English physician (d. 1752).

SCHEELE, KARL WILHELM, "Traité chimique de l'air et du feu par Charles-Guillaume Scheele." Part I, Paris, 1781; Part II, Paris, 1785.

SCHEELE, KARL WILHELM, "Mémoires de chymie de M.C.W. Schéele," 2 parts in one, Paris, 1785.

Extracted from the Memoires of the Royal Academy of Science of Stockholm and translated into French by Madame Guyton de Morveau, in part.

INGENHOUSZ, JAN, "Nouvelles Expériences et Observations sur divers objets de physique," 2 vols., Paris, 1785–89.

Volume I contains much Franklin material. Chapter 17 of Volume II is a French translation of Franklin's letter to Ingenhousz, on chimneys, written at sea in August, 1785, and contains the woodcut illustration of the Foyer de Straffordshire.

INGENHOUSZ, JAN, "Expériences sur les Végétaux, etc.," Vol. 2 only, Paris, 1789.

The book was a presentation copy from the author, who wrote on one of its pages, "For Mr. Jefferson, ministre Plenipot of the United States of America, from the Author," and asked Jefferson to take one copy to Franklin, one to the American Philosophical Society, and one to Samuel Vaughan, Jr. Before receiving it Jefferson had read the original English version, (published in 1779, ten years before the author translated it into French).

Ingenhousz (1730–99) was a member of the Royal Society of London and the American Philosophical Society.

LAVOISIER, ANTOINE LAURENT, "Traité elementaire de chimie, présent dans un ordre nouveau et d'après les découvertes modernes," etc., 2 vols., Paris, 1789. Plates by Madame Lavoisier.

CHAPTAL, JEAN ANTOINE CLAUDE, COMTE DE CHANTELOUP, "Elémens de Chymie," 3 vols., Paris, 1796.

Jefferson admired Chaptal and owned a copy of the latter's practical book on winemaking, for which he praised the writer.

FORONDA, VALENTIN DE, "Lecciones ligeras de Chimica," Madrid, 1791.

("Easy Lessons in Chemistry.") Probably presented to Jefferson by the author. A dialogue between father and son.

Foronda was Spanish Consul in Philadelphia (1802–09) and corresponded with President Jefferson concerning the Spanish Colonies in North America.

EWELL, THOMAS, "Plain discourses on the laws or properties of matter," etc., New York, 1806.

A book on the principles and applications of chemistry, bearing a letter of approval in the preface from Thomas Jefferson, to whom the book is dedicated. Ewell wrote Jefferson, asking if he thought it proper to write an up-to-date chemistry book, in plain language for all to understand. Jefferson replied:

. . . but of the importance of turning a knolege of chemistry to

[4] The inventory of this Jefferson library is known as the "1815 Catalogue." The inventory of another library which he assembled later is known as "The 1829 Catalogue, by Nathaniel Poor," and is reproduced later in this study.

[5] ROSENBACH, A. S. W., "A Book Hunter's Holiday," p. 144, and SOWERBY, E. MILLICENT, "Catalogue of the Library of Thomas Jefferson," Vol. I, Library of Congress, 1952, p. xi

household purposes I have been long satisfied. [T]he common herd of philosophers seem to write only for one another. [T]he chemists have filled volumes on the composition of a thousand substances of no sort of importance to the purposes of life; while the arts of making bread, butter, cheese . . . remain totally unexplained. Chaptal has lately given to the chemistry of wine making. [T]he late Dr. Pennington did the same as to bread, & promised to pursue the line of rendering his knolege useful to common life; but death deprived us of his labors.

Ewell (1785–1826) became a naval surgeon through the influence of Jefferson. His father was a friend and classmate of Jefferson's at William and Mary, where this book was used as a text.

ADET, PIERRE AUGUSTE, "Leçons élémentaires de chimie," etc., Paris, 1804.

Adet was ordered by the government to compile this elementary work, a book for students at the lycée. Jefferson's copy was presented by the author, who wrote that he hoped that the book would find favor in Jefferson's eyes. Thomas Ewell, to whom Jefferson sent the book, changed his mind about translating and publishing it in this country, holding that it contained scarcely any new thing "in matter or arrangement."

Chemistry Tracts: (Bound together.)

(*a*) ARCHER, JAMES, "An Inaugural Essay on Effects, and Modus Operandi of the Carbonates of Lime, Magnesia, and Potash; in the cure of General and Local Diseases," Philadelphia, 1804.

(*b*) PRIESTLEY, JOSEPH, "The Doctrine of Phlogiston established, and that of the Composition of Water refuted," Philadelphia, 1803.

This was a presentation copy to President Jefferson, who wrote Priestley, thanking him. Dr. Priestley, in this contribution defends the phlogiston theory against its enemies.

MARCET, JANE, "Conversations on Chemistry; in which the elements of that science are familiarly explained and illustrated by experiments . . ., Second edition. Vol. I. On simple bodies; [Vol. II. On compound bodies]," London, 1807.

Jane Marcet (1769–1858, née Haldimand) was a famous Swiss-English writer of books (for little children), which became classics in her day. She also wrote "Conversations" on political economy, natural philosophy, and vegetable physiology.

WATSON, RICHARD, "Chemical Essays," 5 vols., London, 1784.

BAUMÉ, ANTOINE, "Chymie Expérimentale et Raisonnée," (Contains an engraved portrait frontispiece of Baumé), 3 vols., Paris, 1773.

Baumé (1728–1804) was the well-known French pharmacist.

FOURCROY, ANTOINE FRANCOIS DE, "Elémens d'histoire naturelle et de chimie," etc., 4 vols., Paris, 1786.

MACQUER, PIERRE JOSEPH, "Dictionnaire de Chimie," etc., 4 vols., London, 1778.

CRAWFORD, ADAIR, "Experiments and Observations on Animal Heat, and the Inflammation of Combustible Bodies; being an Attempt to resolve these Phenomena into a General Law of Nature," London, 1788.

This book was sent by Benjamin Vaughan to Jefferson, who replied that he had long desired it.

Crawford (1748–95) was a British physician and chemist. He was a Fellow of the Royal Society and a member of the Philosophical Societies of Dublin and Philadelphia.

DOBSON, MATTHEW, "A Medical Commentary on Fixed Air . . . with an appendix on the Efficacy of the Solution of Fixed Alkaline Salts saturated with Fixible Air, in the Stone and Gravel. With large Additions and several new Cases. By William Falkoner, M.D.," London, 1787.

Dobson, a Fellow of the Royal Society and a native of Liverpool, died in 1784. Falconer also a Fellow of the Royal Society and an M.D., edited the work and added the Appendix.

ROULAND, "Tableau historique des propriétés et des phénomènes de l'air, considéré dans ses différens étâts et sous ses divers rapports," Paris, 1784.

SIGAUD DE LA FOND, JEAN RENÉ, "Essai sur différentes espèces d'air-fixe, ou de gas, pour servir de suite et de supplément aux Elémens de Physique du même Auteur," Paris, 1785.

Sigaud de La Fond (1740–1810) was a French physicist, member of the Royal Society of Montpelier, the Academy of St. Petersburg, Florence, Valladolid, etc.

LA METHERIE, JEAN CLAUDE DE, "Essai analytique sur l'air pur, et les différentes espèces d'air," Paris, 1785.

PENINGTON, JOHN, "Chemical and economical essays, designed to illustrate the connection between the theory and practice of chemistry, and the application of that science to some of the arts and manufactures of the United States of America." [It has the slogan]: "It is a pity so few chemists are dyers and so few dyers chemists." Philadelphia, 1790.

It is probably the earliest book on the subject of chemistry by an American. Jefferson approved most heartily of this book, (and Penington's practical writings on bread), deploring the fact that death had deprived us of more such works by the author.

Penington (1768–93) was a Philadelphia physician and a member of the American Philosophical Society. He organized the first chemical society in the United States (1789). He died in the yellow fever epidemic.

SMITH, THOMAS PETERS, "A Sketch of the Revolutions in Chemistry," Philadelphia, 1798.

JACOBS, WILLIAM STEPHEN, "The Student's Chemical Pocket Companion," Philadelphia, 1802.

JACOBS, WILLIAM STEPHEN, "Experiments and observations in urinary and intestinal calculi," Philadelphia, 1801.

GUYTON DE MORVEAU, LOUIS BERNARD, BARON, "Traité des moyens de désinfecter l'air, de prévenir la Contagion, et d'en arrêter les progrès," 3rd ed., Paris, 1805.

This is a treatise on disinfecting the air, preventing contagion, and checking its progress. It contains plates and side notes relative to yellow fever. It was a Jefferson favorite. He wrote to Caspar Wistar, calling it "a work of great interest to cities subject to infection, to hospitals, vessels, and indeed to the country inhabitants," and offering it to him. Jefferson sent a copy and a set of the de Morveau "permanent and portable apparatus for disinfection" to the American Philosophical Society, hoping that some of its physician-members would experiment with it, and find the process "of great public value."

Guyton de Morveau (1737–1816) was an attorney and a chemist, well-known figure in the French and Chemical Revolutions.

CAZALET, JEAN ANDRÉ, "Théorie de la Nature," Bordeaux, 1796.

This was a presentation copy from the author and bears an inscription from him. Cazalet (1750–1821) was professor of physics and chemistry at Bordeaux.

COOPER, THOMAS, "The Introductory Lecture of Thomas Cooper, Esq., Professor of Chemistry at Carlisle College, Pennsylvania," Carlisle, Pa., 1812.

Of this book Jefferson wrote: "I have just entered on the reading of it and perceive that I have a feast before me."

Thomas Jefferson was highly pleased with Cooper's discussion of the applications of chemistry to brewing, distilling, making of bread, butter, cheese, soap, and industry, in general.

"Go on in all your good works without the eye of suspicion and distrust with which you are viewed by some and be assured that you are justly esteemed by the impartial mass of our fellow citizens and by none more than myself," Jefferson wrote.

Jefferson was not a professional scientist, but rather an enthusiastic and intelligent amateur. Lacking time to concentrate on any one field, he encouraged others to do so and, by lending his enormous prestige to the cause, he was a highly influential factor in showing his fellow Americans the value of science. He kept searching for applications of chemistry and the other sciences which would add to the comfort and happiness of mankind (yet found himself ridiculed and accused of "neglect of his proper duties"—even of atheism). Such scientific investigations as he made were careful and exact, and he was not inclined to the hasty conclusion.

He wanted not one or a few but all sciences to be developed for the ultimate good of his fellow men, writing (to President Willard, of Havard, in 1789) that science would become the cornerstone of the Republic and that our educational institutions could thus do justice "to our country, its productions, and its genius. It is the work to which the young men you are forming should lay their hands. We have spent the prime of

our lives in procuring them the precious blessings of liberty. Let them spend theirs in showing that it is the great parent of science and virtue, and that a nation will be great in both always as it is free."

Acknowledgments

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A Simple Technique for Semimicro Volumetric Gas Analysis

The technique of injecting a liquid into a gas chamber by rolling a mercury globule over a film of the liquid in a capillary tube may be used to advantage in volumetric gas analysis. It is also useful in analysis where a gas is used as a reagent. The percentage by volume of a major component of a gaseous mixture can be determined by measuring the decrease in length of a column of the gas, trapped between two mercury globules in a uniform bore glass tube, upon exposure to a suitable absorbent solution.

A simple and interesting example of the technique is the determination of the per cent by volume of oxygen in the atmosphere. The author has consistently obtained a value of 20.9 ± 0.1% by the procedure outlined below.

A 40-cm column of air is trapped between two mercury globules in a 2-mm i.d. glass tube about a meter long. The tubing is placed flat on the table top and the distance between the globules is measured to the nearest mm while the column is near the right end of the tube. The column is then drawn almost to the left end of the tube and a few drops of pyrogallol absorbent solution[2] is introduced next to the left mercury globule by means of a medicine dropper with a drawn out stem. The globules are next drawn about 30 cm toward the right and then forced back toward the left end of the tube. The left globule rolls over a film of the pyrogallol solution which is thus exposed to the entrapped gas column. A 20-cm length of this solution film between the globules will rapidly absorb the oxygen in the tube. After a few minutes exposure, the globules are again drawn into the right side of the tube until the left globule has rolled completely over the dark film of pyrogallol solution and the space between the globules is free of absorbent solution. The distance between the globules is again determined, after a few minutes to allow thermal equilibration, and the per cent by volume oxygen is computed. (It should be noted that any carbon dioxide present also reacts with the pyrogallol, and this is included in the "percentage of oxygen" thus obtained). The ratio between the decrease in length and the original length of the column is the fraction by volume of oxygen in the atmosphere. Care should be taken to avoid contact of pyrogallol solution with the skin, and the usual precautions should be observed in handling the small quantity of mercury.

The sample tube may be filled with other gas samples by mild aspiration or low pressure flow through a fine capillary. The mercury globules may be introduced by placing a small quantity of mercury in the rubber tubing between the sample container and the measuring tube and raising the rubber tubing so that the mercury blocks the flow of gas and is forced into the measuring tube. Most of the conventional gas absorbent solutions have low vapor pressure at room temperature and do not react rapidly with mercury. If the absorbent solution has an objectionably high vapor pressure, this may be determined by the method previously described by the author[3] using an inert gas in the measuring tube, and an appropriate correction may be applied to the final length measurement. When it is desired to test for more than one component in the mixture, the measuring tube should terminate in a small spherical glass joint to which a series of absorption tubes may be attached in succession, care being taken to prevent the absorbents from coming near this joint.

[1] Graduate student and N. S. F. Faculty Fellow, 1960–61.

[2] VOGEL, ARTHUR I., "A Textbook of Quantitative Inorganic Analysis Theory and Practice," 2nd ed., Longmans, Green and Co., New York, **1951**, p. 802.

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The Third Law of Thermodynamics, the Unattainability of Absolute Zero, and Quantum Mechanics

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Statements of the third law of thermodynamics current in textbooks (and courses) are mostly expressed in a form derived from the Nernst heat theorem, i.e., in terms of the vanishing of the entropy or entropy change for reactions in the limit of the absolute zero of temperature. For example:

In any isothermal process between condensed phases

$$\lim_{T \to 0} \Delta S = 0$$

This form, though simple and general, is unfortunately untrue, e.g., liquids, glasses, and solid solutions mostly do not obey it. This is usually pointed out in succeeding paragraphs. Other common formulations which make some or all of these restrictions explicit, are:

The absolute value of the entropy of a pure solid or a pure liquid approaches zero at 0°K (1):

$$\lim_{T \to 0} S = 0$$

Transitions between solids at the absolute zero leave the entropy unchanged (2).

The entropy of all pure crystalline solids may be taken as zero at the absolute zero of temperature (3).

Even the restrictions implied by "pure" and "crystalline" are not sufficient to insure the applicability of the law; for these reasons the Lewis and Randall statement (4) is often used:

If the entropy of each element in some crystalline state be taken as zero at the absolute zero of temperature, every substance has a finite positive entropy, but at the absolute zero of temperature the entropy may become zero, and does so become in the case of perfect crystalline substances.

Even this formulation, which is already involved is, however, not strict enough; otherwise perfect crystals composed of molecules possessing different isotopes, nuclear spin orientations, or those capable of different orientations do not necessarily obey it. It can be argued, of course, that the adjective "perfect" already excludes these cases, but this interpretation puts a very much more restrictive meaning on the term than would be implied in any but the present context. Sometimes, in order to preserve the simplicity of the statement, a "permissive" formulation is used:

The entropy of most pure crystalline solids may be taken as zero at the absolute zero (5).

Most students, even sophisticated ones, when confronted with these formulations, draw the erroneous conclusion that the third law is a very weak law in the sense that it either makes a very weak statement of general applicability, or else a strong positive statement applying, however, in only a vanishingly small number of cases. They certainly find it hard to understand, why, as implied by its name, it is juxtaposed to the two most general and sweeping natural laws known, the first and second laws of thermodynamics. This lack of understanding is both symbolized and abetted by the relatively large number of pages devoted in most textbooks to explanations of the applicability of and exceptions from the third law (sometimes qualified as "apparent" third law). These pedagogic difficulties can readily be avoided, if quite a different approach is used to express the third law: that of the principle of the unattainability of the absolute zero (6).

It is impossible by any procedure, no matter how idealized, to reduce any assembly to the absolute zero in a finite number of operations.

This principle was first stated in 1912 (7). The big advantage of this approach is that no qualification whatsoever is necessary; also the form is now quite similar to that of usual statements of the first law (impossibility of creating energy) and the second law (impossibility to convert heat completely into work isothermally or: impossibility of the flow of heat from a colder to a warmer body without accompanying change). All three laws in this form can be looked upon as direct statements of an overwhelming amount of experimental evidence.

It can be shown easily that the vanishing of the entropy change at the absolute zero (Nernst's heat theorem) follows necessarily from the principle of unattainability of the absolute zero, wherever the former applies (8).

There exists one possibility for confusion if the principle of unattainability of the absolute zero is taken as the fundamental statement of the third law, and this is in connection with the consequences of the second law concerning the dependence on temperature for the efficiency of heat pumps as refrigeration engines. This can, however, be turned into a pedagogic advantage by a clear discussion which brings out the interesting interrelation of the second and third law and quantum mechanics.

One formulation of the second law in terms of the efficiency of a refrigerating engine is as follows:

$$\frac{w}{q} \geq \frac{T_2 - T_1}{T_1} = \frac{\Delta T}{T_1} \qquad (1)$$

where T_2 and T_1 are the temperatures of the upper and lower heat reservoirs, respectively, and w is the amount of work that has to be done to withdraw the amount of heat q from the lower reservoir. The equality sign refers to the limit of an ideal (reversible) engine; it is seen that for any real engine more work has to be done

to remove the same amount of heat, i.e., the efficiency is smaller. If we apply this to the problem of cooling a system, it shows that the amount of work necessary to remove a given amount of heat tends toward infinity as the temperature of the system to be cooled tends to zero; at first sight this might imply that the cooling efficiency drops to zero (and this is often stated) and hence that the absolute zero is unattainable. However, this conclusion is not necessarily warranted, since it is the efficiency in terms of the temperature rather than the heat change which is the determining factor. In order to find the temperature change caused by a certain work expenditure, one has to examine the relation between heat taken up (q) and the temperature change per cycle (dT) which is given by

$$q = -q_r = -C(T)dT \tag{2}$$

where q_r is the heat lost from the reservoir and $C(T)$ is its heat capacity dE/dT. Note that q_r and dT are negative.

Hence,

$$\frac{w}{-dT} \geqslant \frac{\Delta T C(T)}{T_1} \tag{3}$$

or

$$-dT \leqslant \frac{wT_1}{\Delta T C(T)} \tag{3'}$$

As can be seen from this equation, the temperature drop goes to zero as the temperature of the system to be cooled tends to zero even in the ideal case, as long as $C(T)$ remains finite; thus in this case the absolute zero seems unattainable.

This can be clarified by using equation (3) to calculate the total work required to reach the absolute zero starting from an initial temperature T_i ($\neq 0$). This work is

$$w_{\text{total}} \geqslant -\int_{T_i}^{0} \frac{(T_2 - T)\,C(T)}{T}\,dT \tag{4}$$

If $C(T)$ is a constant, C, then equation (4) becomes

$$w_{\text{total}} \geqslant C\left(T_2 \ln \frac{T_i}{0} - T_i\right) \tag{5}$$

i.e., the necessary work tends to infinity, even in the ideal case; if, however, $C(T)$ is not constant but goes to zero with temperature, even mildly, then the situation is different. Let

$$C(T) = \alpha T^{\epsilon},\ \epsilon > 0 \tag{6}$$

then

$$w_{\text{total}} \geqslant \alpha T^{\epsilon}{}_i \left(\frac{T_2}{\epsilon} - \frac{T_i}{\epsilon+1}\right) = C(T_i)\left(\frac{T_2}{\epsilon} - \frac{T_i}{\epsilon+1}\right) \tag{7}$$

which may be finite.

We can look at the situation from yet another point of view; let us calculate the temperature as a function of the number of cooling cycles, each one using the same amount of work, w. Let $T(n)$ be the temperature of the system after n cooling cycles starting with $T_i \equiv T(O)$.

Then, again from (3'),

$$-dT \leqslant \frac{wTdn}{(T_2 - T)C(T)} \tag{8}$$

and, by integration,

$$T_2 \int_{T(0)}^{T(n)} \frac{C(T)}{T}\,dT - \int_{T(0)}^{T(n)} C(T)dT \geqslant -nw \tag{9}$$

which determines $T(n)$.

Again, if $C(T)$ is a constant, C, then, solving for $T(n)$

$$\ln \frac{T(n)}{T_i} \geqslant \frac{CT(n) - CT_i - nw}{CT_2} \geqslant -\frac{CT_i + nw}{CT_2} \tag{10}$$

since $T(n) \geqslant 0$. Hence,

$$T(n) \geqslant T_i\, e^{-(T_i/T_2)}\, e^{-(nw/CT_2)} \tag{11}$$

i.e.,

$$T(n) \geqslant A\, e^{-Bn} \tag{11'}$$

This clearly means that the approach to zero temperature is at best exponentially asymptotic, and it cannot be reached in a finite number of cycles, even in the ideal case.

If the heat capacity, however, is not constant but given by (6), then integration and subsequent rearrangement gives

$$T(n)^{\epsilon}\left(\frac{T_2}{\epsilon} - \frac{T(n)}{\epsilon+1}\right) \geqslant -\frac{nw}{\alpha} + T_i{}^{\epsilon}\left(\frac{T_2}{\epsilon} - \frac{T_i}{\epsilon+1}\right) \tag{12}$$

Here the right hand side will become zero for a finite n and this will mean (since $\{(T_2/\epsilon) - [T(n)/(\epsilon+1)]\} > 0$ always) that the temperature of the system can be reduced to zero, and will be so in the ideal case after a number of cycles

$$n = \frac{\alpha}{w} T_i{}^{\epsilon}\left(\frac{T_2}{\epsilon} - \frac{T_i}{\epsilon+1}\right) = \frac{C(T_i)}{w}\left(\frac{T_2}{\epsilon} - \frac{T_i}{\epsilon+1}\right) \tag{13}$$

The total amount of work done to reach the absolute zero, nw, is, of course, identical with that calculated directly, equation (7).

We see then that for a constant heat capacity the *second* law of thermodynamics already rules out the attainment of the absolute zero but that this is not so for a heat capacity vanishing (even weakly) with temperature.

Now let us look at the proof that shows that the vanishing of the entropy change at the absolute zero follows necessarily from the principle of the unattainability of the absolute zero (*8*).

The proof is based on the finiteness of the integral $\int_0^{T'} [C(T)/T]dT$ where T' is any finite temperature. If $C(T)$ vanishes with temperature, e.g., can be represented by equation (6), then the integral is indeed finite (equal to $(\alpha/\epsilon)T'^{\epsilon}$); if, however, $C(T)$ is a constant, the integral becomes infinite for any $T' \neq 0$ and the proof does not hold.

To summarize, we see that for a constant heat capacity the unattainability of the absolute zero is a direct consequence of the second law; nothing, however, can be deduced from the latter concerning entropy changes at the absolute zero and their vanishing has to be postulated separately.

If the heat capacity vanishes, however, the second law in itself does *not* preclude the attainment of the absolute zero; if the unattainability is postulated (independently), it is then equivalent to the vanishing of entropy differences at the absolute zero.

Now, according to classical theory $C(T)$ should indeed be independent of temperature (equipartition). This must be so for any model, no matter what its details, in which the system can take up energy continu-

ously. If we, however, postulate the basic concept of a quantum theory, i.e., discreteness of energy uptake, then

$$\lim_{T \to 0} C(T) = 0 \qquad (14)$$

This is so since in the limit of very low temperatures where kT is vanishingly small compared to ΔE, the finite energy difference between the ground state and the next higher state of the system, the energy of the assembly of systems will be independent of temperature change since not enough energy will be available to raise any system out of the ground state. This holds again independent of any particular model.

Actually, the details of quantum mechanics show that $C(T)$ goes to zero quite fast (as T^3 for Debye solids, and exponentially in all other cases) and this is also in excellent agreement with experiment.

We can summarize these conclusions in the following way:

Classical Systems:

Second law implies unattainability of absolute zero; vanishing of entropy change at 0°K (Nernst heat theorem) has to be postulated (in correct form).

Quantal Systems:

Second law does not imply unattainability of absolute zero. Unattainability of absolute zero implies Nernst heat theorem (in correct form) and vice versa.

One minor point remains to be cleared up: In what way and by what means does the third law affect the conclusions obtained from the second law for systems with vanishing heat capacity, i.e., equations (7) and (13), and prevent an ideal engine from reducing the temperature of a system to zero?

Equation (7), which is completely general, is not affected at all, i.e., the total work that would be expended in the reduction of the temperature to zero would indeed be finite under all circumstances. Equation (13), however, showing that this could be done in a finite number of cycles is based on the assumption that the same amount of work, w, is done in each cycle. It can be shown, however, that $w = \Delta T \Delta S$ and the work done in each cycle will vanish with the entropy differences and hence the number of operations necessary to reduce the temperature to the absolute zero will still be infinite. A simple and clear discussion of these points can be found in the introductory part of a published lecture by F. E. Simon (*9*).

It is often stated, and quite correctly, that thermodynamics is so general that it is independent of any theory of the structure of matter and can, therefore, conversely not be used to decide between rival theories, as, e.g., classical and quantal. The relation of the second and third laws of thermodynamics set forth above form a very striking, simple, and instructive "exception" to this rule.

This is also very interesting from the historical point of view; the first formulation of the Nernst heat theorem preceded and was independent of the detailed development of quantum mechanics.

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(7) Nernst, W., *Berlin. Sitzungsber.*, p. 134 (**1912**).

(8) For a clear and detailed discussion of these connections, see Fowler and Guggenheim, *op. cit.*; Moore, *op. cit.*; also Simon, F. *Z. Phys.* **41**, 806 (**1927**).

(9) Simon, F. E., "Low Temperature Physics," Academic Press, Inc., New York, **1952**, pp. 2–6.

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Austin 12

The General Equation for the Equivalence Point Potential in Oxidation-Reduction Titrations

A survey of thirty-four quantitative analysis textbooks, both at the elementary and advanced levels, revealed that no general equation for the equivalence point potential in oxidation-reduction titrations has been described. In four of these texts the calculation was completely ignored. In another thirteen an equation for the equivalence point potential was not given but the potential was calculated for a simple titration, commonly for the ferrous-ceric system. In twelve books, $a\text{Red}_1 + b\text{Ox}_2 = a\text{Ox}_1 + b\text{Red}_2$ was given as the general titration reaction, and the equation

$$E_{\text{eq. p.}} = (bE_1^\circ + aE_2^\circ)/(a + b) \qquad (1)$$

given as the general equation for the equivalence point potential. In several of these the explicit statement was made that equation (1) is a *completely* general expression. On the other hand, Pierce, Haenisch, and Sawyer[1] recognize that equation (1) may be used only when the reactants are substances for which the numbers of moles are the same for the oxidized and reduced forms. Blaedel and Meloche[2] also realize this fact, and derive the expression for the equivalence point potential in the titration of iron(II) sulfate by potassium dichromate which shows that the potential is a function of the concentration of the reactants. Michaelis[3] also mentions titration curves in which the equivalence point potential is dependent upon the initial concentration of the substance to be titrated. In the standard reference of potentiometry, Kolthoff and Furman,[4] a more general reaction is mentioned in connection with equilibrium concentrations, but in the chapter on oxidation-reduction titrations only equation (1) is given. Lingane[5] treats a much more complicated system, the titration of iodide ion with ceric ion, in which he takes into account the iodine-triiodide equilibrium and the solubility of iodine in aqueous solutions. However, he does not give an equation for the general case.

Described below is the derivation of a general equation for the equivalence point potential which is valid for all oxidation-reduction titrations in which no additional equilibria are extant. The significance of this equation is not primarily its pragmatic aspect, but rather its indication that the equivalence point potential is in general a function of the concentration of the reactants and not a simple weighted average of the standard (or formal) potentials, as is usually assumed.

[1] Pierce, W. Conway, Haenisch, Edward L., and Sawyer, Donald T., "Quantitative Analysis," 4th ed., John Wiley & Sons, Inc., New York, **1958**, p. 424.

[2] Blaedel, W. J., and Meloche, V. W., "Elementary Quantitative Analysis: Theory and Practice," Row, Peterson & Company, Evanston, Illinois, **1957**, pp. 716f.

[3] Michaelis, L., "Physical Methods of Organic Chemistry," 2nd ed., Vol. I, Part II, Interscience Publishers, Inc., New York, **1949**, p. 1775.

[4] Kolthoff, I. M., and Furman, N. Howell, "Potentiometric Titrations," John Wiley & Sons, Inc., New York, **1926**, pp. 57f, pp. 106f.

[5] Lingane, J. J., "Electroanalytical Chemistry," 2nd ed., Interscience Publishers, Inc., New York, **1958**, pp. 141–147.

Derivation

Consider the titration of a reductant Red_2 by an oxidant Ox_1, assuming first that no additional species (e.g., hydrogen ion) are involved in either half-reaction. The potential throughout the titration is governed by the half-reactions of species (1) and (2):

$$a\ \text{Ox}_1 = b\ \text{Red}_1 - xe \qquad E_1^\circ \qquad (2)$$

$$c\ \text{Ox}_2 = d\ \text{Red}_2 - ye \qquad E_2^\circ \qquad (3)$$

The titration reaction is

$$ya\ \text{Ox}_1 + xd\ \text{Red}_2 = yb\ \text{Red}_1 + xc\ \text{Ox}_2 \qquad (4)$$

The potential during the titration is governed by the Nernst expression:

$$E_1 = E_1^\circ - \frac{RT}{xF} \ln \frac{[\text{Red}_1]^b}{[\text{Ox}_1]^a} \qquad (5)$$

$$E_2 = E_2^\circ - \frac{RT}{yF} \ln \frac{[\text{Red}_2]^d}{[\text{Ox}_2]^c} \qquad (6)$$

where brackets denote activities (or concentrations if E° is the formal potential).

At equilibrium, $E_1 = E_2$, and the familiar expression:

$$\ln \frac{[\text{Red}_1]^{yb}[\text{Ox}_2]^{xc}}{[\text{Ox}_1]^{ya}[\text{Red}_2]^{xd}} = \ln K = \frac{xyF}{RT}(E_1^\circ - E_2^\circ) \qquad (7)$$

is obtained.

At the equivalence point (stoichiometric point):

$$xc[\text{Red}_1]_{\text{eq. p.}} = yb[\text{Ox}_2]_{\text{eq. p.}} \qquad (8)$$

and,

$$ya[\text{Red}_2]_{\text{eq. p.}} = xd[\text{Ox}_1]_{\text{eq. p.}} \qquad (9)$$

Applying (8) and (9) to (5) and (6):

$$E_{\text{eq. p.}} = E_1^\circ - \frac{RT}{xF} \ln \frac{(yb/xc)^b[\text{Ox}_2]^b_{\text{eq. p.}}}{(ya/xd)^a[\text{Red}_2]^a_{\text{eq. p.}}} \qquad (10)$$

and,

$$E_{\text{eq. p.}} = E_2^\circ - \frac{RT}{yF} \ln \frac{[\text{Red}_2]^d_{\text{eq. p.}}}{[\text{Ox}_2]^c_{\text{eq. p.}}} \qquad (11)$$

Finally, multiplying (10) by x and (11) by y and adding, with simplification:

$$E_{\text{eq. p.}} = \frac{xE_1^\circ + yE_2^\circ}{(x + y)} - \frac{RT}{(x + y)F} \ln \frac{(yb/xc)^b[\text{Ox}_2]^{b-c}_{\text{eq. p.}}}{(ya/xd)^a[\text{Red}_2]^{a-c}_{\text{eq. p.}}} \qquad (12)$$

A more convenient and useful formula is obtained

in terms of only a single reactant at its initial concentration. By solving (8) and (9) for $[Red_1]_{eq.\ p.}$ and $[Ox_1]_{eq.\ p.}$ and applying to the equilibrium expression for the reaction (7), one obtains:

$$K = \frac{(yb/xc)^{yb}[Ox_2]^{yb+zc}_{eq.\ p.}}{(ya/xd)^{ya}[Red_2]^{ya+xd}_{eq.\ p.}} \quad (13)$$

Solving this expression for $[Red_2]_{eq.\ p.}$,

$$[Red_2]_{eq.\ p.} = \left|\frac{(yb/xc)^{yb}[Ox_2]^{(yb+zc)/(ya+xd)}_{eq.\ p.}}{(ya/xd)^{ya}K}\right|^{1/(ya+xd)} \quad (14)$$

and introducing into equation (12) yields, after some simplification:

$$E_{eq.\ p.} = \frac{xE_1^\circ + yE_2^\circ}{(x+y)} - \frac{RT}{(ya+xd)F}\ln\left[\frac{(yb/xc)^{db}}{(ya/xd)^{da}}K^{(a-d)/(x+y)}[Ox]_2^{\frac{yb}{q}-ca}_{q.\ p.}\right] \quad (15)$$

If the initial concentration of $[Red_2]$ is C_i, then at the equivalence point (assuming K is quite large, as is usually the case in titrations):

$$[Ox_2]_{eq.\ p.} = (c/d)C_i\frac{V}{V+v} \quad (16)$$

where V is the initial volume and v is the volume of titrant added.

Introducing (16) into (15) and simplifying one obtains:

$$E_{eq.\ p.} = \frac{xE_1^\circ + yE_2^\circ}{x+y} - \frac{RT}{(xd+ya)F}\frac{(a-d)}{(x+y)}\ln K - \frac{(db-ca)RT}{(xd+ya)F}\ln C_i\frac{V}{V+v} - \frac{RT}{(xd+ya)F}\ln(y/xd)^{(b-a)d}\times(b^b/a^a)^d(cd)^{ca} \quad (17)$$

For titrations where additional species are involved in either or both half-reactions:

$$a\ Ox_1 + lL = b\ Red_1 + mM - xe,\ E_1^\circ \quad (18)$$

$$c\ Ox_2 + pP = d\ Red_2 + qQ - ye,\ E_2^\circ \quad (19)$$

where L, M, P, and Q are substances involved in the half-reactions which are neither oxidized nor reduced (e.g., hydrogen ion, water, etc.), the derivation is quite similar. The general equation in this case is:

$$E_{eq.\ p.} = \frac{xE_1^\circ + yE_2^\circ}{x+y} - \frac{RT}{(xd+ya)F}\frac{(a-d)}{(x+y)}\ln K - \frac{(db-ca)RT}{(xd+ya)F}\ln C_i\frac{V}{V+v} - \frac{RT}{(xd+ya)F}\ln(y/xd)^{(b-a)d}\times(b^b/a^a)^d(cd)^{ca} - \frac{RT}{(x+y)F}\ln\frac{[M]^l_{eq.\ p.}[Q]^q_{q.\ p.}}{[L]^l_{eq.\ p.}[P]^p_{q.\ p.}} \quad (20)$$

where $[M]_{eq.\ p.}$ represents the activity or concentration of M at the equivalence point, etc.

Applications

Case I: a = b = c = d = 1

This represents the usual titration (e.g., MnO_4^- versus Fe^{+2}).

$$MnO_4^- + 8H^+ + 5e = Mn^{+2} + 4H_2O \qquad E_1^\circ$$

$$Fe^{+3} + 1e = Fe^{+2} \qquad E_2^\circ$$

$$l = 8,\ x = 5,\ y = 1,\ m = p = q = 0$$

$$E_{eq.\ p.} = \frac{5E_1^\circ + E_2^\circ}{6} + \frac{RT}{6F}\ln[H^+]^8_{eq.\ p.},$$

and the equivalence point potential is a simple combination of the E°'s and pH.

Case II: a = c = d = 1 ≠ b

Titrations involving one half-reaction in which the number of moles of oxidized and reduced forms of the reactants are not equal, such as Fe^{+2} versus $Cr_2O_7^=$:

$$Cr_2O_7^= + 14H^+ + 6e = 2Cr^{+3} + 7H_2O \qquad E_1^\circ$$

$$Fe^{+3} + 1e = Fe^{+2} \qquad E_2^\circ$$

a = 1, b = 2, c = 1, d = 1, l = 14, x = 6, y = 1, m = p = q = 0

Here the equivalence point potential is:

$$E_{eq.\ p.} = \frac{6E_1^\circ + E_2^\circ}{7} + \frac{RT}{7F}\ln[H^+]^{14} - \frac{RT}{7F}\ln{}^2/_3 - \frac{RT}{7F}\ln C_i\frac{V}{V+v}$$

where C_i is the initial concentration of iron(II). In this case only the ln K term disappears.

Case III: a = c = 1 ≠ b ≠ d

Titrations involving two half-reactions in which the number of moles of oxidized and reduced forms of the reactants are not equal, such as $S_2O_3^=$ versus I_3^-:

$$I_3^- + 2e = 3I^- \qquad E_1^\circ$$

$$S_4O_6^= + 2e = 2S_2O_3^= \qquad E_2^\circ$$

For the titration reaction, in the form of equation (4):

$$2I_3^- + 4S_2O_3^= = 6I^- + 2S_4O_6^=$$

$x = y = 2,\ b = 3,\ d = 2,\ l = m = p = q = 0$, then

$$E_{eq.\ p.} = \frac{E_1^\circ + E_2^\circ}{2} + \frac{RT}{24F}\ln K - \frac{RT}{2F}\ln 4.50 - \frac{5RT}{6F}\ln C_i\frac{V}{V+v}$$

where C_i is the initial concentration of $S_2O_3^=$ and assuming that the iodine is almost completely in the I_3^- form and is present in such small concentration that the iodine remains soluble. Expressing K in terms of the E°'s [equation (7)] and at a temperature of 25°C,

$$E_{eq.\ p.} = \frac{E_1^\circ + E_2^\circ}{2} + \frac{E_1^\circ - E_2^\circ}{6} - 0.019 - 0.05\log C_i\frac{V}{V+v}$$

Since $E^\circ_1 = 0.536$ v versus normal hydrogen electrode and $E_2^\circ = 0.08$ v versus N. H. E.,[6] the equivalence point potential is about 180 mv more positive (assuming 0.01 M initial thiosulfate concentration and negligible volume change, e.g., titration with 0.1 M I_3^-) than the potential calculated from the weighted average of the E°'s for alone. More important, the equivalence point potential changes 50 mv for every tenfold change in C_i.

Conclusion

The treatment given above will hold for all oxidation-reduction titrations in which no additional equilibria are extant. It is seen that the calculated equivalence

[6] LATIMER, WENDELL M., "Oxidation Potentials," 2nd ed., Prentice-Hall, Inc., Englewood Cliffs, N. J., 1952.

point potential will involve concentration terms for many common titrations (e.g., I_3^-, Br_2, $Cr_2O_7^=$, $C_2O_4^=$, $S_2O_3^=$, H_2O_2). Although in many cases these corrections are small, and are of little consequence experimentally (because end-point potentials are usually determined empirically), they are significant from a theoretical point of view and may be important in scaling macro-titrations to micro levels.

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An Aid to Weighing by Swings

To get maximum balance performance, weighing must be done by the method of swings. To obtain swings of optimum magnitude by mere release of the arrestment requires some skill or several attempts. Fanning with the hand is simple, but a beginner can cause serious damage if he strikes the moving parts. A useful alternative is to make a single careful release and to initiate or control the swings with the balance case closed.[1,2] This may be done quite simply by the electromagnetic device shown in Figure 1. Construction of such a device affords a simple student project.

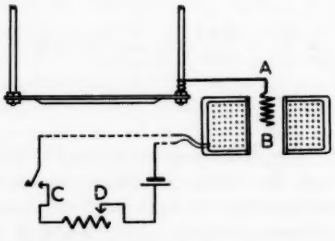

Figure 1. Solenoid and control circuit.

Armature A is made by plaiting together six 20-cm lengths of 36-gauge soft iron wire. A 5-turn coil about 5 mm in diameter and 10 mm long is then formed on one end, while the other is twisted around the right hand outer pan support rod as shown. Acting as a compensator, an identical armature is similarly attached to the left hand pan; the zero of the balance is then adjusted.

Solenoid B has about 500 turns of 28-gauge insulated copper wire, the ends of which are soldered to subminiature flexible connecting leads. The solenoid may be wound on a short length of corkborer or other thin brass tubing about 15 mm in diameter and enclosed within a pair of plastic bottle-caps placed mouth-to-mouth. With some balances, the flexible leads may be passed out of the case through the hole in the baseplate provided to operate the pan-arresting levers. The leads are connected to a single penlight cell through a pushbutton C and a preset resistor D of maximum resistance about 25 ohms. These parts are mounted within a small flat box so that the pushbutton may be easily operated.

The solenoid housing rests upon, or is lightly cemented to, the balance baseplate so that the solenoid is coaxial with the right-hand armature. With the arrestment released and the pointer at mid-scale, about one turn of the armature should be outside the solenoid, as shown. Continuous depression of the pushbutton then causes the pointer to travel smoothly across the scale to a quite reproducible limit determined by the resistor setting, as indicated by curve I, Figure 2. This limit is but slightly affected by loading the balance; a comparison of curves II and III appears to indicate that the change is mainly due to the decreased sensitivity of the loaded balance.

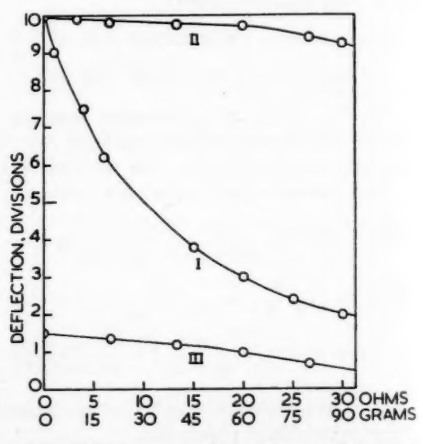

Figure 2. Relationship between resistor setting or load and steady deflection. Curve I (upper scale), unloaded balance; II (middle scale), resistor set at zero; III (lower scale), sensitivity of balance, divisions per mg.

In practice, the pushbutton is usually briefly depressed to augment or diminish the swing resulting from normal arrestment release. It is obvious that completion of the circuit when the armature is *receding* from the solenoid will *reduce* unduly large swings. The maximum current is less than 0.1 amp and is drawn for a few seconds at a time. Replacement of the cell thus depends mainly on shelf life.

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Chemical Mnemonic Devices

A mnemonic device is an aid to memory, and chemists, who have a lot to remember, have developed such devices for use all the way from the color changes of litmus to complex thermodynamic functions. Some have been published, but there must be many good ones that are in oral circulation only. Several of these were sent in response to requests appearing in the JOURNAL OF CHEMICAL EDUCATION and other journals, and the author wishes to take this opportunity to thank all who contributed. The following is a selection of those that were not found in print, along with the name of the contributor, who may or may not be the originator.

"Leo the lion says GER." Loss of Electrons is Oxidation; Gain of Electrons is Reduction. (Lee Meriwether, Montgomery Bell Academy, Nashville, Tennessee.)

$K_4Fe(CN)_6$—$K_3Fe(CN)_6$. The sound of the formula when read can be linked to the name—K-four refers to the ferro, and K-three refers to the ferri compound.

The symbols of the elements in the two short periods can be written in order to form the nonsense words: Helibebc-nofne and Nenamgal-sipscla. (Arcot Viswanathan, Loyola College, Madras, India.)

"I dine 1:27." The atomic weight of iodine is 127. (T. Lloyd Humberstone, London, England.)

E. J. H. Birch, College of Technology, Art, and Commerce, Oxford, England, bases mnemonic aids on the old parlor game of "Telegrams," and suggests the following for the elements of the lanthanide series: "Last Case Pineapples Not Produced Since Elizabeth Got Terrible Dysentery Having Eaten Two Yours Lucy."

"Do what your oughter—pour the acid in the water." (Glenn Powers, Northeast Louisiana State College, Monroe, La.)

"Oh, My Sugar Gets Away." Dicarboxylic acids, oxalic through adipic.

"Mama Eats Potatoes But Papa Hates Hash." Alkanes, methane through heptane. (Amy Le Vesconte, Flora Macdonald College, Red Springs, N. C.)

"Troy Girls Can Flirt And Other Queer Things Can Do." Moh's hardness scale. (William G. Kessel, Indiana State Teachers College, Terre Haute, Indiana.)

"Roy G. Biv." The colors of the rainbow. (Louis H. Dunlop, McKeesport High School, McKeesport, Pa.)

"Oh, how transcendentally angelic it is to tickle Cis." In angelic acid the methyl groups are trans, in tiglic acid they are cis. (Robert E. D. Clark, Cambridgeshire Technical College, Cambridge, England.)

The mnemonic devices that have been published appear in different ways—as short articles, in letters to the editor, and as small items in columns devoted to various topics. Since many of these are not included in the indexes and so are not easily found, the following list of published mnemonic devices cannot be considered to be complete.

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Elements essential to plant nutrition—GORDON, ROBERT B., *Am. Biology Teacher*, **12**, 160–61 (1950).
Essential amino acids—PATTON, A. R., *Chem. and Eng. News*, **27**, 371 (1949).
Space arrangement of fumaric acid—COX, GERALD J., *Chem. and Eng. News*, **33**, 3368 (1955).

Generally, with a published mnemonic device the origin is not indicated, and it might be assumed that it was original with the author or that its origin was unknown. In a few cases, however, some particular person is given credit. A device for Maxwell's thermo-

dynamic relations is attributed to Professor H. A. Taylor of New York University. The code sentences for the electrochemical series that start "Peter Saw Carl," are attributed to the late J. H. Walton of the University of Wisconsin (*1*). The code sentence "Oh My Such Good Apple Pie, Sweet As Sugar" for the dicarboxylic acids, oxalic through sebacic, is attributed to Alfred Burger of the University of Virginia (*2*), and to the late Professor E. Jewett Moore of MIT (*3*).

There is objection to the use of mnemonic devices on the grounds that there is too much stress on memorizing, and there are disadvantages in their use where the things to be memorized are subject to change. And some teachers have their students make up their own devices (*4*, *5*).

Some mnemonic devices are themselves humorous or ludicrous, but a further touch of humor was added when the word "mnemonic" was misspelled in one of the published devices. Promptly, two letters to the editor appeared, each offering a mnemonic device for the spelling of the word mnemonic (*6*, *7*).

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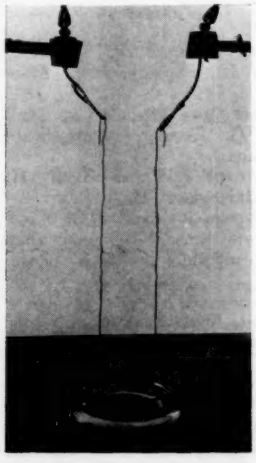
Demonstrating the Relative Polarity of Non-Conducting Liquids

The rough correlation between dielectric constant and the polarity (dipole moment) of a molecule makes it possible to use determinations of dielectric constants as an indication of the polarity of a molecule. Normally, methods used for the determination of dielectric constants require complicated apparatus and an understanding of rather advanced principles. It thus becomes impossible to demonstrate differences in polarity of bonding to a high school or college freshman chemistry class.

The apparatus to be described is based on the principle that an increase in the dielectric constant of the medium causes a decrease in the force of attraction between charged particles. The "charged particles" consist of two plastic beads about 1 cm in diameter. A bead is threaded on one end of each of two pieces of #18 bare copper wire about 32 cm long. (If the fit is loose, the wire may be doubled or plastic cement may be used to give a tight joint.) A piece of aluminum foil about 4 cm square is wrapped tightly around each bead so that electrical contact is made with the wire. An open hook is formed at the non-bead end of each of the wires by bending them about 2 cm from the end. These wire and bead electrodes are then suspended from stirrups made of heavy bare copper wire supported in the hole of a #5 or larger one-hole rubber stopper held by a buret clamp. The electrodes of a Wimshurst machine are then connected to the stirrups making sure that the leads are not grounded. A shallow glass dish is filled with the liquid to be tested to sufficient depth so that the beads can be submerged without touching the bottom of the dish. By adjusting the ringstands and buret clamps, the beads are lowered into the liquid. The electrostatic machine is cranked and attraction or lack of it is noted. The distance between the beads is then varied so that the maximum distance at which attraction occurs may be noted. An alternate method of measurement is to keep the distance between the beads constant (3 or 4 mm) and note the relative amount of cranking of the electrostatic machine necessary to cause attraction.



The author has used carbon tetrachloride, chloroform, acetone, and water, the maximum distance of attraction varying from about 7.5 cm for carbon tetrachloride to 0 for water. It is suggested that volatile, inflammable liquids of very low dielectric constant such as benzol not be used because of the danger of sparking outside the liquid causing a fire. While the writer has not experienced fires with either chloroform or acetone, a fire extinguisher should be available during the demonstration.

This apparatus can also be used in explaining the role of the solvent in the electrolytic dissociation process and the variation of the capacity of a condenser with the dielectric constant of the insulating medium

Proceedings of the

California Association of Chemistry Teachers

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Los Angeles 7

New Horizons in Elastic Polymers

Elastic polymers or elastomers are the rubbers, natural and synthetic. Natural rubber is found in trees, shrubs, vines, and small plants, chiefly in the Amazon Valley. Practically all the natural rubber is obtained from the plantations in Ceylon, Malaya, Indonesia, Indo-China, Thailand, the Philippines, Liberia, and Central America. Recently natural rubber was found in fungi belonging to two of the major classes, Ascomycetes and Basidomycetes (*1*). The latex occurs in tubes of several species of *Lactarius*, and to a lesser extent in *Peziza*. Samples obtained from *Lactarius* were 1.7% on a dry-weight basis, analyzed properly for carbon and hydrogen, and were identified further by comparison of the infrared absorption spectra with a purified sample of *Hevea brasiliensis* (natural rubber). The viscosity average molecular weight was 13,900. Samples were vulcanized by the Peachey process with hydrogen sulfide and sulfur dioxide.

Scientific work on natural rubber was begun only a century and a half ago. In 1826 Michael Faraday helped to establish the fact that the chief constituent of natural rubber is a hydrocarbon having the empirical formula C_5H_8. In 1860 Greville Williams isolated the low boiling fraction from dry distillation and named it isoprene. An effort was made to synthesize rubber before the structure of isoprene was known. G. Bouchardat in 1879 had the "bold idea," as Harries later remarked, that isoprene was the foundation stone of rubber, and by the action of hydrochloric acid he converted it into a rubber-like solid. Questions have been raised about this possible synthesis, and it may be that the isoprene had stood for some time and contained peroxides which are catalysts of polymerization. W. A. Tilden in 1884 obtained isoprene by cracking turpentine and used Bouchardat's method to convert it into a rubberlike mass. Tilden later proposed the correct structural formula for isoprene. It was synthesized in 1897 by W. Euler.

In 1910 the Russian, I. Kondakow, published his work on the polymerization of 2,3-dimethylbutadiene to an "elastic-like rubber" (No. 4 on the Chart.) The monomer boils at 69°C, and I recall with interest that in about 1915 I prepared it and polymerized it to a synthetic rubber with sodium as the catalyst; isoprene and butadiene were difficult to prepare and handle—no dry ice was on the market then.

The polymerizing action of metallic sodium was discovered independently in 1910 by Matthews in England and Harries in Germany. You will remember that the structure of the natural rubber hydrocarbon was the work of Harries through his use of ozone which formed an ozonide which, in turn, on hydrolysis gave levulinic aldehyde. Later work showed natural rubber to be a *cis* form (No. 2 on Chart). In World War I the Germans produced 2350 tons of polymerized dimethylbutadiene, known as "methyl rubber" (No. 4 on Chart.) A long time, two to six months, was required for polymerization. The natural rubber hydrocarbon, *cis*-polyisoprene (No. 2 on Chart) was not synthesized until 1954, when it was announced without details of the method of producing it by the president of the B. F. Goodrich Company. The chemists of the Firestone Tire and Rubber Company accomplished the synthesis at the same time by the use of finely divided lithium on isoprene. The Goodrich product is called "Ameripol SN," and the Firestone product "Coral" rubber. During this present year the Shell Chemical Company put synthetic natural rubber hydrocarbon on the market at 30 cents a pound. It is being manufactured at the rate of 5 tons a day.

The first commercial synthetic rubber was "Thiokol," in 1929, prepared by J. C. Patrick by the reaction of ethylene dichloride and sodium tetrachloride (No. 16 on Chart). It may be the first synthetic rubber prepared from materials other than diene hydrocarbons. It has no unsaturation, is vulcanized by zinc oxide, and is resistant to swelling in oils and solvents, to permeability of gases, and to oxidation. "Neoprene," otherwise known as polychloroprene or poly-2-chlorobutadiene (No. 5 on Chart) announced by the du Pont Company in 1931 is more like natural rubber in its properties than many other synthetic rubbers.

During the 1930's the Germans were busy on the methods they discovered partly in the late 1920's. The sodium rubbers, known as "Buna" rubbers from the first two letters of butadiene and of natrium, were never produced in quantity, but Buna S consisting of 75 parts of butadiene and 25 parts of styrene (No. 6 on Chart) was manufactured by an emulsion system. This synthetic rubber was somewhat like natural rubber in its properties, especially when compounded with carbon black. Buna N, from butadiene and acrylonitrile, later known as nitrile rubber (No. 7 on Chart),

[1] Formerly Director of the TLARGI (The Los Angeles Rubber Group, Incorporated), Rubber Technology Foundation.

was also manufactured in an emulsion. In this country Butyl rubber (No. 11 on Chart) of a very high proportion of isobutylene and very low proportion of isoprene was announced by the Standard Oil Development Company in 1940. Such was the condition when the United States became involved in World War II.

Not much was known of the German work in this country but by means of good hard work and cooperation a better Buna S began rolling out in December, 1943, and soon GR-S as it was called (No. 6 on Chart), reached very high production figures. After the war, conditions were found to lower the temperature of the emulsion from 122° to 41° F and "cold GR-S" was produced. Carbon black was added as a dispersion to the cold GR-S latex, and this made it possible to remove carbon black itself from certain factories. GR-S also was extended with petroleum oil. The government factories were bought by private companies in 1955.

Now we have the silicone rubbers (No. 22 on Chart) with their remarkable properties from very low to high temperatures, the polyacrylates (No. 15 on Chart), the carboxylic rubbers (No. 8 on Chart), Hypalon (No. 10 on Chart), polyesters (Nos. 17, 18 and 19 on Chart), polyurethane rubbers (No. 21 on Chart), Kel-F Elastomers (No. 12 on Chart), Viton A (No. 13 on Chart), and others.[2]

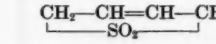
The world production of natural rubber in 1958 was 1,955,000 long tons and of synthetic rubbers in the United States in 1958, 1,056,915 long tons.

Synthetic Rubbers

Mention has already been made of the synthesis of the natural rubber hydrocarbon, *cis*-polyisoprene, and of its commercial production at a selling cost of 30 cents a pound by the Shell Chemical Company. The Goodrich Company, the first to make this synthesis, has now synthesized perdeuterio synthetic natural rubber hydrocarbon (No. 3 on Chart); that is, the synthetic *cis*-polyisoprene with the hydrogen atoms replaced with deuterium atoms (*5, 6, and 7*). The deuterioisoprene boils almost 2°C lower than the regular isoprene. The new isoprene was polymerized in aliphatic and aromatic solvents with titanium tetrachloride and triisobutyl-h_{27}-aluminum as the catalyst mixture. Polymerization is fast. The polymer had 25% of gel, and the soluble portion had a molecular weight of 333,000. The X-ray diffraction pattern of the polymer vulcanized with tetramethylthiuram disulfide, $(CH_3)_2N{\cdot}CS{\cdot}SS{\cdot}CS{\cdot}N(CH_3)_2$, and zinc oxide was superposable over those of natural and synthetic natural rubber hydrocarbon. The density is 1.009 at 25°C.

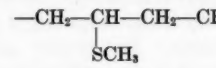
Carbon-14 natural rubber hydrocarbon has been prepared by laboratory biosynthesis (*8*). With an extract of *Hevea brasiliensis* latex containing the natural enzymes, sodium acetate with carbon-14 was converted into natural rubber containing carbon-14.

Natural rubber, *cis*-polyisoprene, and balata, *trans*-polyisoprene (No. 2 on Chart), have each been isomerized to a common structure having a *cis/trans* ratio estimated to lie somewhere between 50/50 and 60/40 by refluxing the solutions of the substances in *o*-dichlorobenzene containing 0.5 g per liter of powdered selenium under nitrogen for 2–5 hours (*9*). It has also been reported that such an isomerization can be obtained by the action of thiol acids, such as thiolbenzoic acid, C_6H_5COSH, and particularly by sulfur dioxide gas, especially by sulfur dioxide from butadiene sulfone,



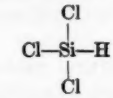
which liberates sulfur dioxide at 130°C (*10*). The sulfone is mixed into the rubber or balata and the mix heated to 140°C. The product is of interest because it has several hundred times the time of crystallization and therefore a lower brittle point than natural rubber.

The addition of mercaptans to natural and synthetic rubbers, polybutadiene, and SBR gives surprising properties in comparison with the starting rubbers



(*11*). Varying proportions chiefly of methyl mercaptan have been used and the products studied. They have a resistance to aging, ozone attack, action of heat, swelling in oils and solvents, and to permeability of gases, all properties increasing with increasing extent of saturation. Furthermore, they have high properties at 400 and 500°F. The ozone resistance is comparable to that of commercially available saturated rubbers.

Cyanosilicone rubbers (Compare No. 22 on Chart) have been prepared by starting with silanic hydrogen which adds to unsaturated nitriles, and the product hydrolyzed and condensed (*12*). Trichlorosilane,



can be added to acrylonitrile, $CH_2{=}CH{-}CN$, and the condensation can be carried on with other organochlorosilanes. The cyanosilicone rubbers have the oil and solvent resistance of the nitrile rubbers together with the wide temperature range of the silicone rubbers—high temperature stability and low temperature flexibility.

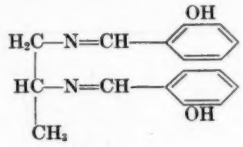
Butyl elastomer containing halogen is prepared by including allyl chloride, $CH_2{=}CH{-}CH_2Cl$, with the isobutylene and isoprene (*13*). They cure rapidly to relatively high states of cure by the action of tetramethylthiuram disulfide or polymethylol resin with zinc oxide. The crosslinks are thermally and chemically stable. The ozone resistance is excellent.

Readers may recall the preparation of Superior Processing or SP Rubber in Malaya by vulcanizing 20 parts of latex, adding this to 80 parts of unvulcanized latex, and coagulating the mixture. The product is especially good for extrusion, since it extrudes smoothly with lower die swell at lower temperatures and higher viscosities, and it calenders with greater conformity to gauge and with control of shrinkage. Now SP Brown Crepe is being produced and soon SP 90 will be available (*14*). SP Brown Crepe starts with a mixture of 80 parts of vulcanized latex and 20 parts of unvulcanized latex—the opposite of the earlier SP Rubber—coagulated to give a crumb which is then mixed with enough

[2] For further information on synthetic and natural rubber not included in this paper, refer to HAUSER, "Synthetic Rubber and Plastics" (*2*); FISHER, "Rubber Plus Chemistry," "Our Versatile Rubbers," all THIS JOURNAL (*3*); "Chemistry of Natural and Synthetic Rubbers" (*3*); and ARNOLD, ET AL., "Organic Isocyanates—Versatile Chemical Intermediates," J. CHEM. EDUC. (*4*).

estate scrap to give a ratio of 20 parts vulcanized and 80 parts unvulcanized rubber. The properties are similar to normal brown crepes and have the superior processing characteristics. SP 90 is prepared from 90 parts of vulcanized latex and 10 parts of unvulcanized latex, coagulated to a crumb. The manufacturer can mix this with any rubber he wishes in his process and obtain superior processing properties.

Viton Fluoroelastomer (No. 13 on Chart) is prepared from vinylidene fluoride and hexafluoropropylene. Two practical curing systems have been found: a blocked diamine and ethylenediamine carbamate; and a combination of hexamethylenediamine carbamate and a diimine retarder-activator such as N,N′-bis-(*o*-hydroxybenzylidene)-1,2-propylenediamine



(*15*). These systems produce very safe processing stocks and vulcanizates with excellent properties. For Viton A Fluoroelastometer it is recommended that a three-part combination be used: ethylene bis-thioglycolate, $HSCH_2COOCH_2CH_2OCOCH_2SH$ (a cross-linking agent), a tertiary amine, and magnesium oxide (*16*). This combination gives good scorch resistance, high tensile strength, and low compression set, but lower age resistance at 550°F. Viton is excellent for high temperature work, ozone resistance, and resistance to swelling in oils and solvents. Viton sells for $10.00 a pound. Viton B is an improved type (*17*).

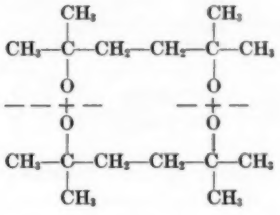
A very interesting new synthetic rubber is an organotin elastomer (No. 23 on Chart) (*18*). Most elastomers contain carbon or silicon in the chain; this one contains tin. Tributyltin oxide and methacrylic acid react readily in benzene to form tributyltin methacrylate, and dibutyltin oxide similarly gives dibutyltin dimethacrylate. The homopolymer of the first one and the copolymer of both of them were prepared in emulsions. The homopolymer is a tough rubbery material and the copolymer is a clear, very elastic material. The tensile strengths of the raw products are approximately 125 lb/sq. in and 400% elongation. Vulcanization was difficult. Zinc oxide decomposes the tin ester structure. But, dibutyltin oxide takes its place, sulfur and dibutyltin dihydride, $(C_4H_9)_2SnH_2$, react as vulcanization agents. The cures were 45 min. at 250°C and 30 min. at 290°C, and the respective results were tensile strength 400 lbs/sq in. and elongation 370%, and 300 lb/sq in. and 250%. The volume change for 24 hours at 25°C in isooctane was 125% and 32.4%, respectively.

Poly(vinyl methyl ether) (No. 14 on Chart) has been vulcanized to a good elastomer by high energy radiation, up to tensile strength 4000 lb/sq in. and over 500% elongation (*19*). The vulcanizate is insoluble but swells in water.

Acetaldehyde has been polymerized in the presence of aluminum oxide to an elastomer with exceptional heat resistance (*20*). The work was done in Japan and its manufacturing cost estimated at 12–15 cents a pound. It lacks unsaturation, and polyacetaldehyde rubber would have to be cured by irradiation or other non-sulfur techniques.

Now the linear copolymer of ethylene and propylene containing 40% of propylene will soon be produced on a large scale by the Montecatini Company in Italy as a synthetic rubber for tires (*21*) (No. 9 on Chart). Their C-23 rubber has a high molecular weight and low specific gravity, 0.85–0.86 g/cm³. Its properties are near to those of natural rubber. Its rebound at 20°C is 75% (Luepke pendulum), and its minimum is reached at −35°C. It has excellent electrical insulating and thermal characteristics.

Vulcanization of polyethylene of both low and high density has been announced by the R. T. Vanderbilt Company by means of Varox which contains 50% of a free-flowing mineral carrier and 50% of 2,5-bis(tert-butylperoxy)-2,5-dimethylhexane (*22*).



This vulcanizing agent acts by possible dissociation at the dotted lines. In press curing considerable distortion is obtained when the sample is removed from the hot mold; cooling under pressure eliminates this condition and provides a satisfactory product.

The tensile strength and elongation of samples, without and with Thermax carbon and vulcanized with 4% of Varox, are from low density polyethylene, 1500 and 2450 lb/sq in. and 600% and 160%, and from high density polyethylene, 3500 and 3640 lb/sq in. and 100% and 90%, respectively.

In discussing polyethylene and polypropylene it seems good to recall the terms used by Giulio Natta of Milan, Italy (*23*), for the different structures: tactic comes from the Greek word *tatto*, I order, meaning ordered; eutactic, well ordered; atactic, not ordered; isotactic, from *isos*, equal; *tatto*, I put in order; ordered polymer; ordered in such a way that when passing along a single chain from one monomeric unit to the subsequent one, there is found repetition of the unit configuration. It is usually eutactic. Syndiotacticity, from three Greek words, *syn*, together; *dyo*, two; *tatto*, I order. A syndiotactic polymer is formed from macromolecules whose monomeric units are asymmetric and ordered in such a way that, when passing along the chain from one unit to the subsequent one, there is found a repetition of position and structure, but inversion of the steric configuration.

The polymers from the simplest and cheapest unsaturated hydrocarbons, ethylene and propylene, are well worth watching.

High Temperature Polymers and Chemical Resistance

The silicone (No. 22 on Chart) and fluoro rubbers (Nos. 12 and 13 on Chart) are considered to have the best properties at high temperatures; that is, very good at 500°F, good at 600°F, and sometimes good for several hours at 700°F. The aviation industry and

ELASTIC POLYMERS

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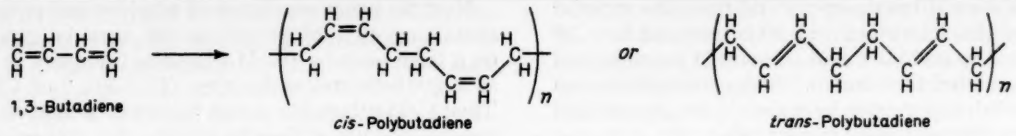

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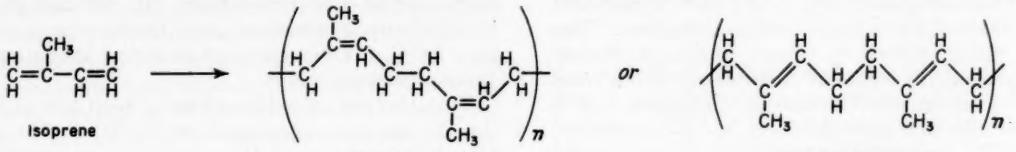

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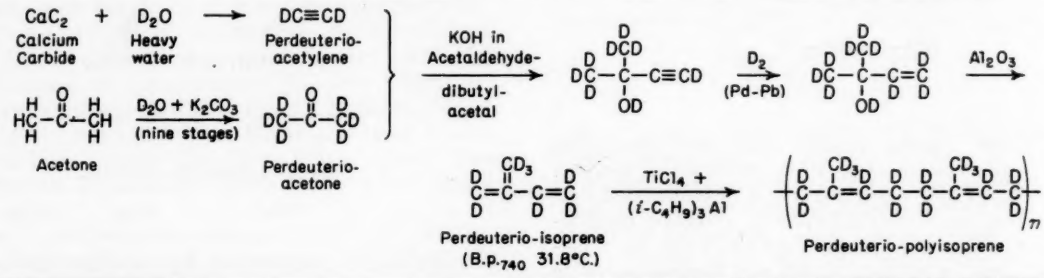

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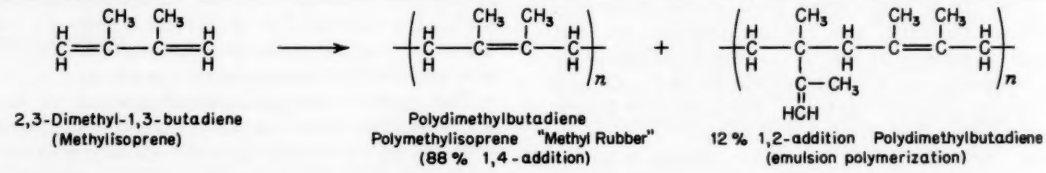

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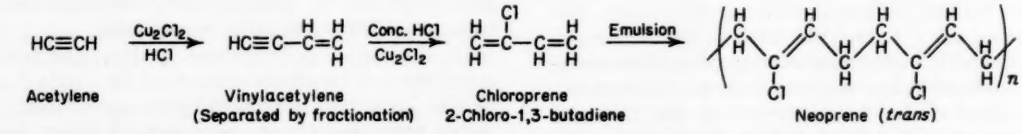

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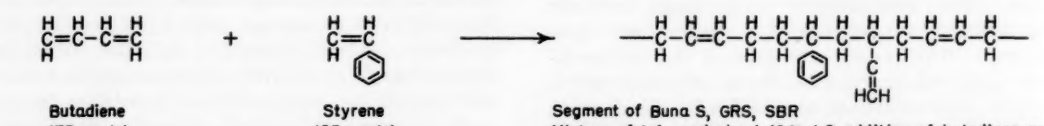
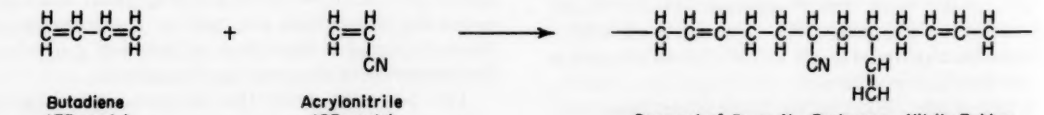


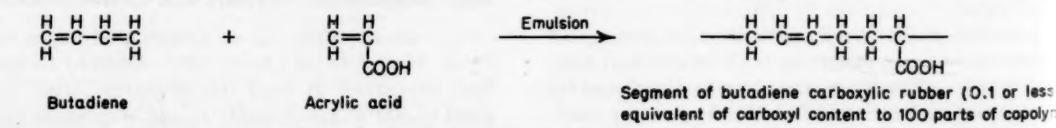
Segment of Buna S, GRS, SBR
Mixture of 1,4- and about 18% 1,2-addition of butadiene, and 22% *cis* and 59% *trans* 1,4-addition forms at 50°C.(122°F) emulsion copolymerization, and 15% *cis* and 68% *trans* at 5°C. (41°F.) emulsion copolymerization.

7



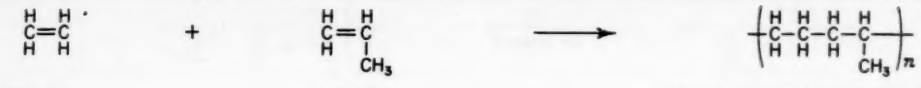
Segment of Buna N, Perbunan, Nitrile Rubber
Chiefly 1,4- and only a low proportion of 1,2-addition; largely *trans*

8



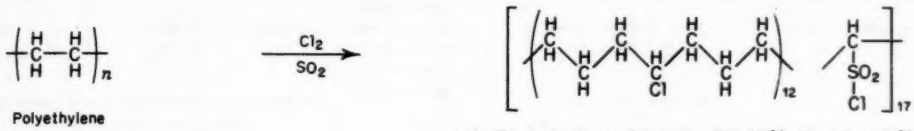
Segment of butadiene carboxylic rubber (0.1 or less equivalent of carboxyl content to 100 parts of copolymer)

9



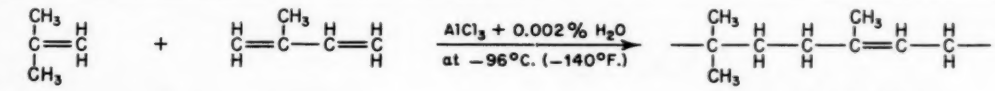
Ethylene + Propylene → Linear copolymer containing 40% of Propylene residues (Montecatini)

10



Polyethylene → (Cl_2, SO_2) Idealized structure of Hypalon (26-29% Cl; 1.3-1.7% S)

11

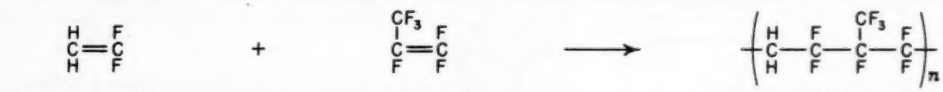


Isobutylene (97 parts) + Isoprene (3 parts) → ($AlCl_3$ + 0.002% H_2O, at −96°C. (−140°F.)) Segment of Butyl Rubber

12

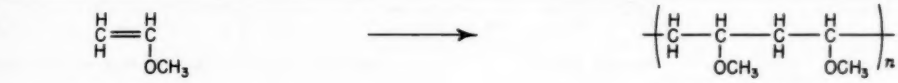
Monochlorotrifluoroethylene + Vinylidene fluoride → Kel-F Elastomer (addition copolymer)

13



Vinylidene fluoride + Hexafluoropropylene → Viton A (addition copolymer)
Fluorocarbon Elastomer 214 is prepared from a 70:30 mixture of vinylidene fluoride and hexafluoropropylene

14



Vinyl methyl ether → Poly (vinyl methyl ether)

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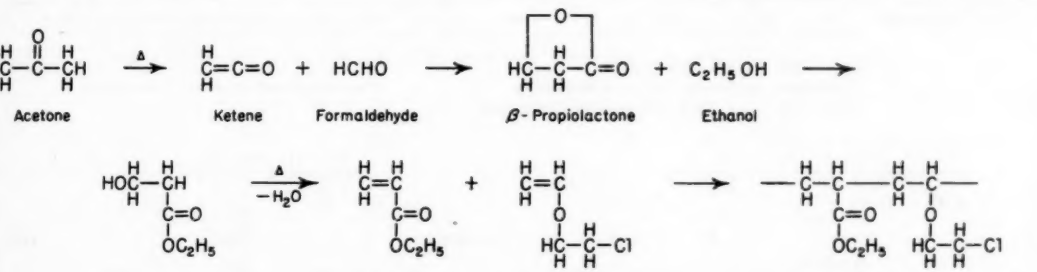
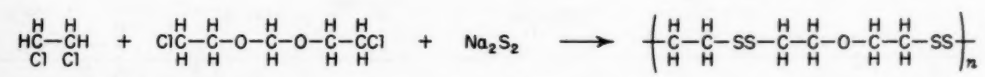


Acetone (Δ) → Ketene + Formaldehyde → β-Propiolactone + Ethanol →

Ethyl hydracrylate (Δ, $-H_2O$) → Ethyl acrylate (95 parts) + 2-Chloroethyl vinyl ether (5 parts) → Segment of copolymer of ethyl acrylate and 2-chloroethyl vinyl ether (Hycar 4021)

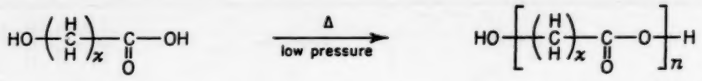
16

Ethylene dichloride + Na_2S_4 → Thiokol A First commercial synthetic rubber
(Position of the fourth sulfur atom not known)



Ethylene dichloride + Dichloroethylformal + Na_2S_2 → Thiokol FA

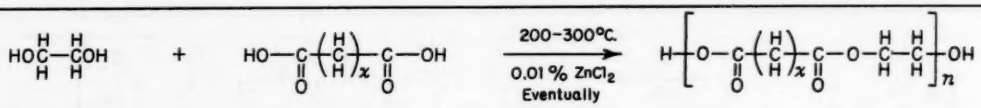
17



ω-Hydroxyalkanoic acid

ω-Hydroxyalkanoic acid polyester
(a condensation polymer)

18



Ethylene glycol

An alkanedioic acid

Polyester of a dibasic acid and ethylene glycol
(Other glycols can be used)
(a condensation copolymer)

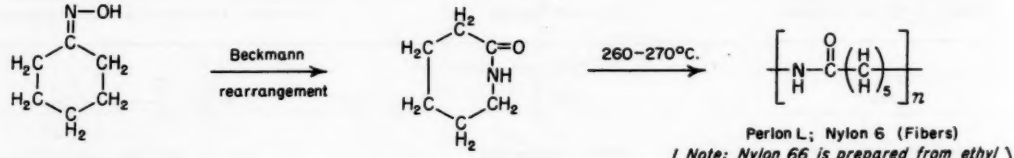
19

Ethylene glycol

Diethyl terephthalate

Polyethylene terephthalate — a polyester fiber
(Dacron; Terylene; Diolen; and Tetoron)
(a condensation copolymer)

20



Cyclohexone oxime

Caprolactam

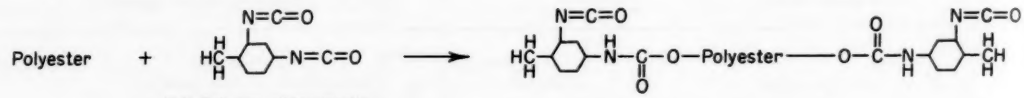
Perlon L; Nylon 6 (Fibers)
(Note: Nylon 66 is prepared from ethyl adipate and hexamethylenediamine)

21

Adipic acid

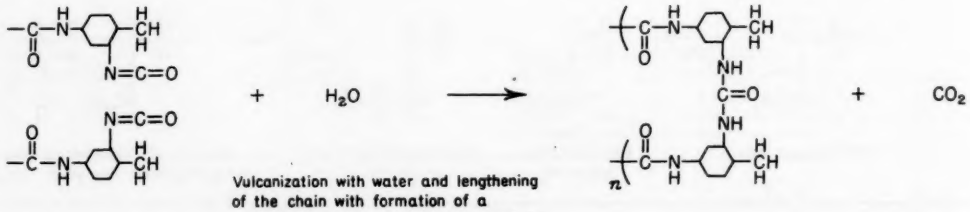
Ethylene glycol

Polyester with 1.2 to 1.8% of free alcoholic hydroxyls

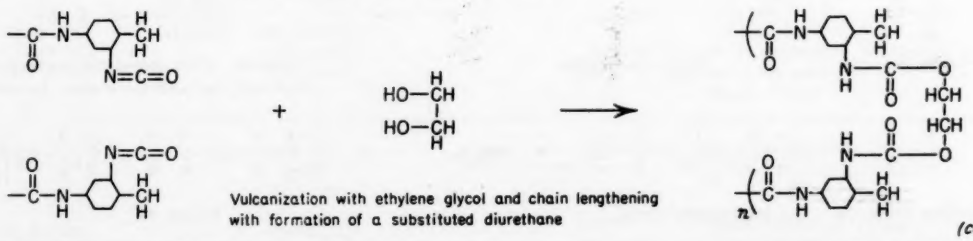


2,4-Tolylene diisocyanate
(Commercial compound (TM) is a mixture of
80% 2,4- and 20% 2,6-tolylene diisocyanate)

Chain-lengthened polyester-diisocyanate



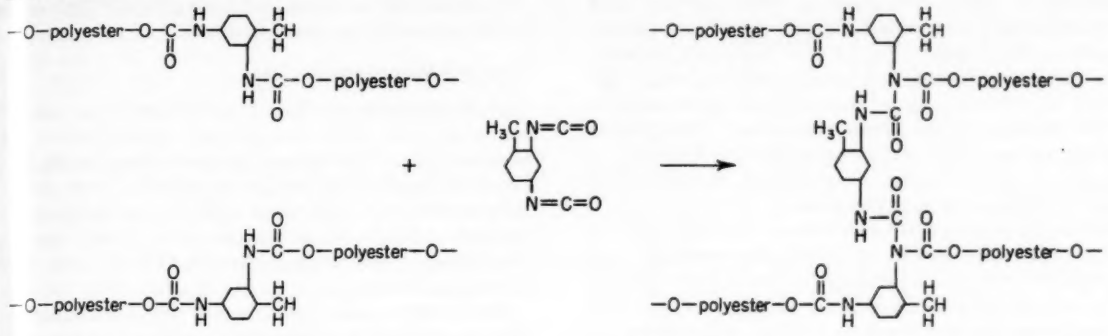
Vulcanization with water and lengthening of the chain with formation of a substituted urea, and elimination of CO_2



Vulcanization with ethylene glycol and chain lengthening with formation of a substituted diurethane

(continued)

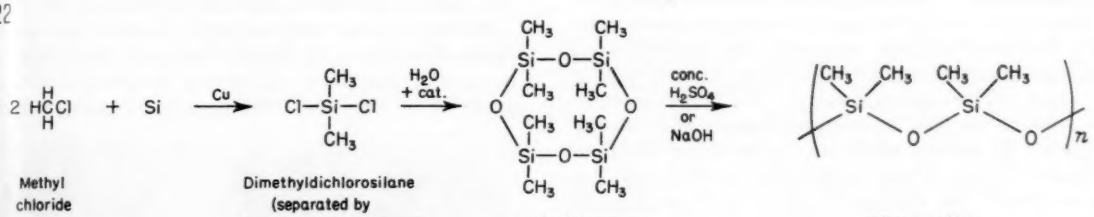
21 *(continued)*



Crosslinking with a diisocyanate

The crosslinked or vulcanized polymer with a diisocyanate

22

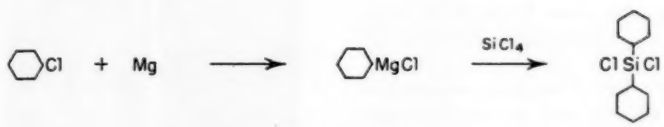


Methyl chloride

Dimethyldichlorosilane (separated by fractional distillation)

Cyclic tetramer

Silicone rubber



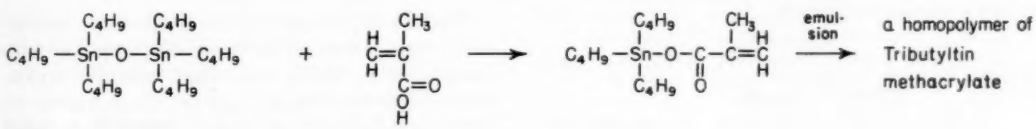
Chlorobenzene

Grignard reagent

Diphenyldichlorosilane

A mixture of about 93% of the dimethyl- and 7% of the diphenyl-dichlorosilane gives a very good silicone rubber with exceptional wide temperature range from −130° to +550°F.

23



Tributyltin oxide

Methacrylic acid

Tributyltin methacrylate

a homopolymer of Tributyltin methacrylate

Dibutyltin dimethacrylate

A mixture of the two esters —emulsion→ a copolymer

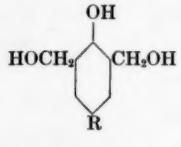
missile programs are calling for rubbers that are very good at 700°F and good at 800°F, but none have been at all satisfactory at 800°F. The cyanosilicone rubbers are good at high temperatures and resist swelling in oils (*12*). The fluoro elastomers are among the best for resistance to the combination of heat, solvents, and chemical attack met in some types of military service (*24–26*). The Vitons (No. 13 on Chart) are prepared from vinylidene fluoride and hexafluoropropylene. The newest jet fighters may be sporting fuel tanks made of solvent-resistant cyanosilicone elastomers. In addition to military uses, the new compounds may be used for adhesives, encapsulating compositions, electric cable components, and sealing compounds.

Kel-F Elastomers 5500 and 3700 are 50:50 and 70:30 copolymers respectively of vinylidene fluoride and monochlorotrifluoroethylene (*24*) (No. 12 on Chart). They possess chemical resistance and thermal stability at high temperatures superior to any other chemical-resistant commercial rubbers.

Fluorocarbon Elastomer 214 (No. 13 on Chart) from 30:70 parts of perfluoropropylene (hexafluoropropylene) and vinylidene fluoride is superior to Kel-F Elastomer No. 3700 after exposure at high temperatures in air, hydrocarbon fuels, motor oil, and diesel oil (*27*). Both elastomers have excellent resistance to red fuming nitric acid at room temperature. No. 214 has superior resistance to swelling in oils and fuels, and to strong oxidizers. It has an advantage of at least 150°F in thermal stability at high temperatures, being serviceable at 500°F for extended periods of time, and in some cases at 600°F for limited periods.

Viton B, a new type of Viton synthetic rubber, shows significant improvement over Viton A at temperatures of 500°–600°F in physical properties and oil and solvent resistance (*17*).

The United States Rubber Company vulcanizes Butyl rubber (No. 11 on Chart) with phenol dialcohol resin and no sulfur (*28*). It then withstands a sustained temperature of 500°F compared to 300°F for standard Butyl, and it will even withstand 700°F for short periods of time. Furthermore, stocks can be processed at higher temperatures than can standard Butyl without scorching. The vulcanizing agent is 2,6-dimethylol-4-hydrocarbylphenol,



or a condensation polymer of it.

Mercaptan adducts of polybutadiene mentioned earlier have exceptional resistance to high temperatures, ozone and γ-radiation (*11*).

Polyurethane Rubbers

The polyurethane rubbers (No. 21 on Chart) are prepared from glycol adipic esters or a polyether, both with free alcoholic hydroxyl groups, and an aromatic diisocyanate (*3, 4* and *29*). Automobile tires are not yet made completely of them, but treads show remarkable resistance to abrasion. They are vulcanized with glycols, diamines, diisocyanates, and water. Polyurethane foams are obtained by vulcanization with water since carbon dioxide is evolved and makes the foam. New mixers, especially a mixer head held in the hand, help in rigid foam dispensing (*30*). Abrasion resistance is high and heat resistance is very good. The uses of polyurethane foams are growing: upholstery, insulation and many small items.

Tires and Miscellaneous Uses

cis-Polybutadiene (No. 1 on Chart) is a potential competitor for both natural and synthetic *cis*-polyisoprene (*31*). Butadiene is much cheaper than isoprene, being only 14.5 cents a pound. It is particularly useful when combined with a small proportion of natural rubber, since the natural rubber prevents crumbling of the polybutadiene and adds tack in the fabrication of tires.

More black masterbatches are being manufactured than heretofore, by combining dispersed carbon black in the SBR latex before coagulation (*32*). Masterbatches made continuously give better processing, better tread wear, and generally better quality to the final compounds than those made by milling.

Passenger tires made entirely of Butyl are now on the market (*33*). They give a smooth, quiet ride, and no squeal; they have the highest hysteresis loss which provides for the best braking and skidding traction.

Tire with replaceable tread rings made by Pirelli, Italy. Left, the casing and rings removed; right, the assembled tire.

Besides rayon and nylon fibers there are in action steel wires (brass or zinc plated), Caprolan—caprolam-based fibers, which somewhat resemble nylon 66 in physical properties but are better at higher temperatures, and Perlon (caprolactam-based fiber, called nylon 6 (No. 20 on Chart) (*34*). Newer developments are polyester group fibers, polyethylene terephthalate (No. 19 on Chart), known as Dacron, Terylene, Diolen, and Tetoron; and polyurethane fibers (No. 21 on Chart). Glass fiber is poor and not used in tires.

The Goodyear Tire and Rubber Company is putting out a truck tire with steel wires (*35*). The Unisteel over-the-road truck tire is built of steel cords instead of fabric plies, and shows up to three times greater tread mileage. The tires are composed of steel cable ply running radially from bead to bead, reinforced by three diagonal steel breaker plies. This construction is said to permit the tread to roll on the road without the wearing, scrubbing movement usually found in over-the-road tires. Flexing is confined to the tire's buoyant sidewalls.

The Pirelli Company, Milan, Italy, has introduced a radically new tire which features replaceable tread rings (*36*). Three such rings are used. They are held in place by the pressure of inflation. Lateral movement is prevented by radial ridges. The tread always rolls, does not slip, and is firmly fixed to inextensible wire reinforcement which forms the base of the rings. The rings do not scuff on the road.

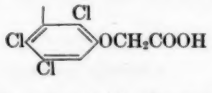
The Dayton Tire and Rubber Company has manufactured tires filled with polyurethane foam rubber in place of air (*37*).

Radiation makes better, longer lasting tires (*38*). Complete vulcanization was obtained with about 4×10^7 rep of radiation, but it is indicated that less than 10^6 rep would be required if the rubber were mixed with 15 per cent of styrene before irradiation. SBR has inherently good resistance to γ-irradiation because of the presence of styrene residues (*39*). Hycar self-sealing fuel cell liner stocks gained the most over-all benefit from the potential anti-rads Akroflex C and quinhydrone. But, except for extruded items, it appears that radiation vulcanization will not be competitive costwise within the next ten years (*40*). Ozone cracking and oxidation are about the same as with sulfur vulcanization; swelling of irradiated elastomers in water is greater, 17–64%. They retain tensile strength better at 212° and 300°F, if tested at the same temperature.

A novel method for obtaining delayed action in vulcanization is the incorporation of accelerators or accelerator activators into artificial zeolites, called molecular sieves (*41*). They are synthetic crystalline alumino-silicate materials, chemically similar to many natural clays and feldspars. Powdered articles are 1–5 microns, are free flowing, and disperse readily. Temperature at which reaction occurs is a function of the volatility of the catalyst; low boiling materials are released at relatively low temperatures, and high boiling materials at higher temperatures.

Fine particles of silica, calcium carbonate, and titanium dioxide in tire treads give tires about 90% of the wear of carbon-black tires. Moreover, the tires can be colored as desired (*42*).

An increase in yield of natural rubber up to 40% has been obtained by coating the bark of mature trees with 2,4,5-trichlorophenoxyacetic acid (*43*).



Chemists in the Goodrich Research Center have developed a continuous mixing device, the Roto-mill (*44*), only 5 in. in diameter, but it can be made larger.

The General Services Administration has begun selling, without replacement, natural rubber from the nation's stockpile, and at prevailing market prices (*45*).

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Report of the New England Association of Chemistry Teachers

Twenty-Second Summer Conference
August 22–27, 1960
University of Maine, Orono, Maine

Host: Irwin B. Douglass, Head of Department of Chemistry, University of Maine
Co-Chairman, Program: Roy J. Gritter, University of Connecticut, Storrs, Connecticut
Co-Chairman, Arrangements: Christie J. Drago, Exeter High School, Exeter, New Hampshire
Conference Secretary: Maurice Bernier, Farmington High School, Farmington, New Hampshire

The popular discussions, movies, and social events for members and families will be continued as at previous conferences. Invited speakers and discussion leaders are as follows:

Monday, August 22, 1960

7:30 P.M. "Space Flight: From Dream to Reality," Dr. Harry O. Ruppe, Redstone Arsenal, Alabama.

Tuesday, August 23, 1960

9:00 A.M. "Asking Students to Use Facts," Dr. Donald C. Gregg, University of Vermont.
"The Chemical Bond Approach," Dr. Laurence E. Strong, Earlham College.

2:00 P.M. Discussion Groups:
"The Teaching of Modern Acid Base Theory," Dr. Donald C. Gregg.
"Chemical Bonds," Dr. Laurence E. Strong.

7:00 P.M. "Progress in Food Preservation," Dr. Harry E. Goresline, Quartermaster Food and Container Institute.

Wednesday, August 24, 1960

9:00 A.M. "Fuel Cells," Dr. J. Weissbart, Westinghouse Electric Company.

2:00 P.M. Picnic, Tidal Falls, Maine.

Thursday, August 25, 1960

9:00 A.M. "Organic and Inorganic Condensation Polymers," Dr. Tod W. Campbell, E. I. du Pont de Nemours and Company.
"Stereospecific Polymers," Dr. Charles G. Overberger, Polytechnic Institute of Brooklyn.

2:00 P.M. "Biochemical Polymers," Dr. Jay S. Roth, Hahnemann Medical College and Hospital.

7:00 P.M. "The State of the Cosmos," Dr. George Z. Dimitroff, Shattuck Observatory, Dartmouth College.

Friday, August 26, 1960

9:00 A.M. "Polysaccharides—A Glimpse at Some Details of Nature's Tapestry," Dr. Irwin B. Douglass, University of Maine.
"Production of Artificial Meteors," Dr. Wendell G. Sykes, Arthur D. Little, Inc.

2:00 P.M. "Recent Changes in the Presentation of a Physical Science," Dr. Noel C. Little, Bowdoin College.

Interested people are urged to write to the Conference Secretary for a complete program and registration details.

Officers for 1960–61

President: Carl P. Swinnerton, Pomfret School

Vice President: Leallyn B. Clapp, Brown University

Financial Secretary: Rev. Joseph A. Martus, S.J., College of the Holy Cross

Recording Secretary: Maryalice C. Moore, Stonehill College

Treasurer: Carroll B. Gustafson, Massachusetts College of Pharmacy

Curator: Ralph E. Keirstead, Connecticut Department of Education

Endowment Fund Trustee (–1963): Avery A. Ashdown, Massachusetts Institute of Technology

Chairman of Divisions:

Central: Harry G. Stubbs, Milton Academy

Northern: Christie J. Drago, Exeter High School

Western: Angela M. Trovato, Branford High School

Southern: Ralph E. Brierley, Cranston High School

At the Executive Committee Meeting on May 13, 1960, Marco H. Scheer, Nashua High School, Nashua, New Hampshire, was elected to honorary membership.

Chem Ed

BOOK REVIEWS

Lehrbuch der Organischen Chemie. Volume 1, Parts 1 and 2

Friedrich Klages, the University of Munich. 2nd ed. Walter de Gruyter & Co., Berlin, 1959. Figs. and tables. 17.5 × 24.5 cm. Part 1, xv + 559 pp., DM 68 and DM 72. Part 2, xv + 519 pp., DM 66.

This is the first of three volumes of a Textbook of Organic Chemistry by Klages. While the second volume is devoted to theories of organic chemistry and the third volume to special topics (*cf.* THIS JOURNAL 36, No. 2, 102, 1959) the present volume is limited to reactions and preparations of organic compounds which are arranged in chapters according to their functional groups, aliphatic and aromatic compounds being treated together. Although the physical properties of many common reagents are described, the main emphasis is on general and specific reactions and correlation of reactivity and properties with the position of a compound in a homologous series. Actual operational aspects of organic reactions are limited to very general and brief discussions of a few important reagents (e.g., $LiAlH_4$) and yields are mentioned only in a handful of cases.

The scope of the book is staggering. Some 3000 reactions are illustrated by equations and schemes and since practically all of the discussions concerning theories and mechanisms are deferred to Volume 2, the reader has to absorb a solid 1000 pages of reactions of common and also uncommon compounds, e.g., three pages devoted to organic compounds of polyvalent iodine.

The book is a heroic example of the paradox concerning the present status of organic chemistry. According to the great Continental tradition an organic chemist knew, among other things, almost everything about organic chemistry. Most well known European chemists were capable of writing (and many did) a treatise covering adequately the whole subject. As a consequence, also, the students were expected to master and retain the contents of these books. It seems that this is no longer possible. The scope of Professor Klage's book as well as his obvious familiarity with even the remote sectors of the whole field is admirable. Still the book can compete neither in scope nor in detail with specialized treatises in any organic field. The author was of course aware of that when he explained in the Introduction that the book was written for a somewhat advanced student of organic chemistry, but as a textbook the work has some serious drawbacks. The broadness of scope, the total separation of reactions from their theory and mechanism (the present volume contains some 1000 or more references to Vol. 2) as well as the lack of operational aspects make the study difficult and tedious. Any teacher of organic chemistry or any practicing chemist must profit greatly from reading the book but, as a teacher, one can only wish for students to whom this work could be recommended.

The printing and paper are excellent; the price is steep even for Americans.

ALEXEJ B. BOŘKOVEC
Virginia Polytechnic Institute
Blacksburg, Virginia

Reviewed in this Issue

Friedrich Klages, Lehrbuch der Organischen Chemie. Volume 1, Parts 1 and 2

Edwin S. Gould, Mechanism and Structure in Organic Chemistry

J. P. Phillips, Automatic Titrators

Edward J. King, Qualitative Analysis and Electrolytic Solutions

J. Smit and *H. P. J. Wijn*, Ferrites

Jean-Jacques Trillat, Exploring the Structure of Matter

Martin Levey, Chemistry and Chemical Technology in Ancient Mesopotamia

Edwin T. Mertz, Elementary Biochemistry

Consultants Bureau, Inc., Soviet Research on the Lanthanide and Actinide Elements, 1949–1957. Parts 1–5

W. P. Jorissen, Induced Oxidation

William H. Corcoran and *William N. Lacey*, Introduction to Chemical Engineering Problems

Lore Lettenmeyer, Editor, Dictionary of Atomic Terminology

Mechanism and Structure in Organic Chemistry

Edwin S. Gould, Stanford Research Institute, Stanford, California. Henry Holt & Co., New York, 1959. x + 790 pp. Figs. and tables. 16.5 × 24 cm. $12.50.

This latest addition to the books dealing with physical organic chemistry is apparently designed primarily for use in a first year graduate course. It is well organized and covers a wide range of topics, many of them with admirable thoroughness. Unfortunately, the treatment of a number of concepts and reaction mechanisms suffers from a lack of rigor. Questionable assumptions are sometimes made and occasionally there is an arbitrary or tacit dismissal of factors potentially as important as those used in explanation. This is particularly true in the first seven chapters which treat introductory structural concepts, acid-base catalysis, and methods of determining reaction mechanisms. The remaining nine chapters deal in detail with various reaction categories, ranging from nucleophilic aliphatic substitution to radical reactions. These are well organized and extensive reviews, largely of the more recent literature through 1958. The interpretations of the original authors are presented with little editing or alteration. Occasionally some of the more pertinent research is omitted from consideration, which certainly is understandable in view of the magnitude of the task of compiling the literature on so many topics.

Examples of instances in which the book may have fallen short of ideality are: (1) the repeated recourse to "single-state reasoning" in discussions of the effect of structure on kinetic or thermodynamic quantities for transitions between two states; (2) an inadequate treatment of absolute rate theory; (3) a superficial treatment of electronic transitions; (4) the absence of any mention that factors other than resonance, e.g., different hybridization of *sigma*-bonds, may contribute to the stabilization energies and shorter carbon-carbon single bond distances, etc., in molecules such as butadiene and propyne; (5) the failure to point out that "crossover experiments" designed to determine whether or not a particular type of reaction is intramolecular are of no value unless the two compounds separately undergo the reaction at nearly the same rate; (6) the failure to recognize that for the reaction path, $A \leftrightharpoons B$ (equilibrium); $B \rightarrow C$, with $[A] \gg [B]$, the observed overall rate constant is independent of the free energy of B; (7) the uncritical acceptance and widespread use of the original unmodified Baker-Nathan theory; (8) some misleading molecular orbital representations.

Although such shortcomings are by no means singular to this particular book, they nevertheless detract from its usefulness as a text for a first year graduate course. The instructor of such a course should find the book to be good source material for his lectures and could profitably assign certain sections for outside study. Furthermore, he may wish to

borrow freely from the many excellent problems found at the end of each chapter. The book has considerable value as a source of references to the original literature on many topics, and for review study for those reasonably versed in the basic concepts and able to read critically.

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Automatic Titrators

J. P. Phillips, University of Louisville, Louisville, Kentucky. Academic Press, Inc., New York, 1959. viii + 225 pp. Figs. and tables. 16 × 23.5 cm. $6.

In this book the author attempts to review exhaustively all instruments for automatic or semiautomatic titration which have been described in the literature or which are available commercially, as of September, 1958.

According to the preface, "Automatic titration is perhaps the only modern instrumental method of analysis in which the point of view of the chemist and training in chemistry remain more useful than an intimate knowledge of physics and electronics. Therefore, the approach used in this book is that of the chemist . . ." It appears, however, that the reader must have more than a cursory familiarity with electronics to follow some of the descriptions in later chapters.

The many instruments discussed are grouped as far as possible according to the method utilized for detection of the end points: potentiometric, amperometric, conductometric, thermometric, and photometric. A chapter is devoted to coulometric titrators. For each general type, the author gives a brief but sufficient discussion of the physical chemistry involved followed by a rather detailed description of specific instruments.

The descriptions seem rather spotty, with much more detail concerning some models than others; this is undoubtedly due in part to the corresponding variety of descriptions in the original sources. There is some repetition; it is difficult to understand why the Beckman KF-2 Aquameter, for example, needs almost identical descriptions on pages 100 and 197.

The chief fault as it appears to the present reviewer is the unsatisfactory drawings, in particular those which are not taken directly from the sources. Several of these are a kind of cross between a flowsheet and an electronic diagram, so that one has to study carefully to determine whether a solid line represents a burette, a flow of liquid, or a wire.

There are a number of questionable statements, only two of which will be mentioned here. On page 107 we find the statement, "Differentiation of a conductometric titration curve gives the shape of the ordinary potentiometric graph with the end point near the inflection." Whether or not one likes this use of the phrase, "ordinary potentiometric graph," one must question the truth of the statement, at least as applied to an *ideal* conductometric titration. Only after reading on as far as page 130 is this matter clarified.

Several references are made to the "slow response of most [potentiometric] electrode combinations," which makes necessary complicated end point anticipation circuits; but, "by contrast with electrodes, most kinds of photocells have practically instantaneous response." Actually electrode lag is usually less significant than delay due to finite stirring time, and this will be present equally for all types of detection.

In spite of its shortcomings, this book should fill a need as a convenient compilation of data from many sources, as all chapters are well documented. The printing and binding leave nothing to be desired. The reviewer only found two minor typographical errors.

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Qualitative Analysis and Electrolytic Solutions

Edward J. King, Barnard College, Columbia University, New York. Harcourt, Brace and Co., New York, 1959. xxi + 641 pp. Many figs. and tables. 16.5 × 23.5 cm. $6.95.

The appearance of still another textbook of qualitative analysis ordinarily evokes little more than a casual comment from those of us engaged in the teaching of this aspect of chemistry. Most "new" texts contain little that is new, and modern versions of older yet reliable volumes are often less desirable. King's recent work, however, is one which deserves special consideration.

The text is designed either for a sophomore course or for the second semester of general chemistry. The principles of electrolytic solution chemistry are treated in the first half of the book, and the laboratory practice of qualitative analysis is covered in the second half. The structure of water and of solutes are considered as well as their interaction to form solutions. Bonding is treated primarily from an electrostatic point of view and a brief excursion is made into ligand field theory. Rates and equilibrium are excellently covered. The effects of interionic forces are carefully considered and the principles of electroneutrality and of material balance are introduced to aid the student in understanding the assumptions usually made in solving simple equilibrium problems as well as to provide the foundation necessary for solving more complex problems. Sufficient depth of material is included so that a very complete and rigorous treatment of the principles of electrolytic solution chemistry can be given at the discretion of the instructor. Each chapter contains pertinent references to the original literature, supplementary readings, and a number of problems designed to encourage the student to think rather than to substitute blindly into equations derived in the text. Many examples, however, of more difficult types of problems are worked out in detail in the text and answers to numerical problems are given in the appendix.

The laboratory part of the book is based on a conventional qualitative scheme of analysis, but one in which thioacetamide is used instead of hydrogen sulfide. The author points out the objections many have raised to the substitution of thioacetamide for hydrogen sulfide but also emphasizes that the study of the mechanism of sulfide precipitations with thioacetamide is one of the frontiers of chemistry. By utilizing the most recent studies as examples of kinetics and homogeneous precipitation the author illustrates the current interest in problems which the student may himself encounter in the laboratory. The text does include, however, the slight modifications in procedure necessary if one wishes to use hydrogen sulfide. The laboratory section also contains an extensive discussion of the chemistry of the elements included in the qualitative scheme based on structural considerations, electrode potentials and equilibrium constants. For each analytical group cross references are made to those sections in the first part of the text which are helpful in understanding the descriptive chemistry of the individual elements.

The author has produced a thoroughly up-to-date text which calls attention to the frontiers of chemistry. The book is extremely well written and deserves the attention of everyone interested in a current approach to the teaching of qualitative analysis and the attendant principles governing the behavior of electrolytic solutions.

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Ferrites

J. Smit and *H. P. J. Wijn*, both of Philips Research Laboratories, Eindhoven, The Netherlands. John Wiley & Sons, New York, 1959. xiv + 369 pp. Figs. and tables. 15.5 × 23.5 cm. $10.

Before commenting on the merits of this book, it might be helpful to cite a few facts gleaned from the book to explain the title. *Ferrites* are defined as magnetic oxides containing iron as the major constituent. They are typified by *magnetite*, the well-known ferromagnetic iron oxide, Fe_3O_4, and the related spinels, $MeFe_2O_4$, where *Me* is one of the divalent ions of the transition elements, Mn, Co, Ni, Cu, and Zn, or Mg and Cd. Another large class of ferrites is derived from ternary mixtures of BaO and Fe_2O_3 with MeO, where *Me* again represents divalent, transition-element ions, or Zn, Mg, or a combination of Li^{I} and Fe^{III}. Crystals based upon the formula $Y_3Fe_5O_{12}$, having a garnet structure, are also ferromagnetic; the yttrium ion can be replaced by those of rare-earth metals, because of nearly identical ionic radii. The replacement of one ion by another in these structures need not be stoichiometric, resulting in compounds with strange looking formulas, like: $Ni_{0.36}Zn_{0.64}Fe_2O_4$; $Ba_3Co_{1.02}Fe^{II}_{0.08}Fe_{24}O_{41}$; and $BaCo_{0.75}Zn_{0.75}Fe_{16.5}O_{27}$. These compounds frequently have vacant lattice sites and the porosity remaining during their preparation also affects their properties. The

(*Continued on page A434*)